EQUIPMENT FOR ANALYZING MINE ATMOSPHERES, WITH SPECIAL REFERENCE TO HALDANE-TYPE APPARATUS

BY H. A. WATSON AND L. B. BERGER

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SUMMARY

This circular, which is a revision and combination of two previous publications,[3] [4] presents information on the different types of equipment that may be used to analyze mine atmospheres, with particular reference to the application and limitations of each type. Such information is frequently requested by mining companies, State mining departments, and other agencies concerned with safety in mining who wish advice regarding methods of analysis of mine atmospheres and the equipment necessary for establishing laboratories for that purpose. Since the Haldane-type apparatus is particularly applicable to the accurate determination of carbon dioxide, oxygen, and combustible gases such as methane in mine atmospheres, that apparatus and the method of operation are described in detail. The circular presents results of a critical study of the accuracy attainable with the Haldane-type apparatus in the determination of methane in concentrations of the order of 0.25 percent, by volume. Analytical procedures involved in the other methods discussed are presented in publications referenced in this circular. Information is given also on the various accessory equipment needed in a laboratory for the analysis of mine atmospheres, and suggestions on laboratory design are included.

INTRODUCTION

The analysis of mine atmospheres plays an important part in promoting safety and maintaining safe conditions in mining operations, particularly in coal mining, where the flammable gas methane presents a continuous hazard in some mines and may be encountered unexpectedly in others.[5] Methane has been encountered also, often unexpectedly and with disastrous results, in noncoal mines and in tunnels under construction.[6 7] The determination of methane is vitally important in underground operations known to liberate this gas because ventilation must be maintained in adequate quantity, and be properly coursed, to dilute and remove the gas as it is liberated. Of equal importance is the search for and detection of methane, even in trace amounts, in mines not hitherto suspected of being gassy, as experience has proved that in many such mines the liberation of methane may increase suddenly and without warning, creating a definite hazard and frequently resulting in disaster.

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[3] Berger, L. B., and Schrenk, H. H., Bureau of Mines Haldane Gas Analysis Apparatus: Bureau of Mines Inf. Circ. 7017, 1938, 24 pp.

[4] Berger, L. B., and Schrenk, H. H., Laboratory Equipment for the Analysis of Mine Atmospheres: Bureau of Mines Inf. Circ. 7441, 1948, 18 pp.

[5] Forbes, J. J., and Grove, G. W. (rev. by McElroy, G. E., Watson, H. A., Coggeshall, E. J., Dornenburg, D. D., and Berger, L. B.), Mine Gases and Methods for Detecting Them: Bureau of Mines Miners' Circ. 33, 1954, 82 pp.

Other conditions that must be considered in respect to underground atmospheres are accumulations of carbon dioxide, depletion of the oxygen content of the air, and the possible presence of toxic gases such as carbon monoxide and oxides of nitrogen.

Because of the diverse nature of the constituents of mine atmospheres, and the various concentrations in which these constituents may occur, no one type of apparatus is suitable for their determination under all conditions that may be encountered in underground operations. If analytical results of usable accuracy are to be obtained, equipment and methods must be selected that are most appropriate for study or examination of the particular situation that exists. The following text discusses these matters in respect to composition of mine atmospheres, methods of sampling, description of analytical apparatus, and methods of procedure.

TYPES OF ANALYSES THAT MAY BE REQUIRED IN DETERMINING THE COMPOSITION OF MINE ATMOSPHERES

The analysis of mine atmospheres may be divided into two general classes with respect to the locations at which the atmospheres exist, namely, in ventilated and unventilated places.

Analysis of the Air of Ventilated Places

In coal mines and in some other underground operations the percentage or concentration of methane in the air of ventilated places is of chief concern because of the potential hazard of explosion. The oxygen and carbon dioxide contents of the air are important also in that significant reductions in oxygen or increases in carbon dioxide may affect the health and efficiency of persons at work in such atmospheres.

The air of ventilated working places also may be contaminated by noxious or poisonous gases that are produced or liberated during mining. Carbon monoxide may be introduced into the air when explosives or internal-combustion engines are used or by leaks from sealed fire areas. The toxic oxides of nitrogen may be produced by explosives and are present in the exhaust gases of internal-combustion engines.

The following data are cited in regard to the concentrations or percentages of these different gases that must be considered in analyzing mine atmospheres:

The Federal Coal Mine Safety Act[8] contains the provision that "all active underground working places in a mine shall be ventilated by a current of air

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[6] Harrington, D., and Denny, E. H., Gases That Occur in Metal Mines: Bureau of Mines Bull. 347, 1931, 21 pp.

[7] Harrington, D., and Ash, S. H., Some Essential Safety Factors in Tunneling: Bureau of Mines Bull. 439, 1941, 61 pp.

[8] Federal Coal Mine Safety Act: Title I, May 7, 1941, Public Law 49, 77th Congress; Title II, July 16, 1952, Public Law 552, 82d Congress.

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containing not less than 19.5 per centum of oxygen, not more than 0.5 per centum of carbon dioxide, and no harmful quantities of other noxious or poisonous gases."

This act also states, in substance, that if 0.25 percent or more of methane is found by air analysis in any open workings of a coal mine within the purview of the act, that mine shall be subject to the provisions of the act relating to the use of permissible equipment.

In regard to the toxic gases, it is generally considered that 0.01 percent by volume of carbon monoxide is the maximum concentration permissible in the air of working places in which exposure does not exceed 8 hours daily. The similar maximum for total toxic oxides of nitrogen is 0.0025 percent (25 parts per million, by volume), although a limit of 5 parts per million has been suggested for nitrogen dioxide.9/

From the foregoing it is evident that the quality of the air of working places must be examined carefully to meet these requirements and that the methods used in analyzing the air must be quite accurate and sensitive if analytical results of any value are to be obtained. For example, if the return air of a coal mine actually contains 0.20 percent methane, it would be meaningless to analyze this air by a method whose accuracy is no better than 0.2 to 0.3 percent, because the results might be in error by an amount equal to or greater than the actual percentage of methane present. If the methane content of the air, as determined by analysis, is to be used in conjunction with a measured air-quantity value to calculate volume of methane liberated by the mine in a given time, the calculated result will be of little or no value unless an analytical method of maximum accuracy is used in determining the methane.

Similarly, if carbon monoxide is to be determined in the air of working places from the standpoint of possible effects upon persons at work in these places, the analytical method must be sensitive to at least 0.01 percent of carbon monoxide.

Methods suitable for analyzing the air of ventilated mine workings are described in a following section.

Analysis of Atmospheres of Unventilated Places

The term "unventilated places" refers to (a) face areas or dead ends through which the ventilating air is not coursed, (b) open, unventilated, abandoned sections, and (c) the areas behind fire seals or gas seals. The atmosphere in such places may contain considerable percentages of carbon dioxide and abnormal accumulations of nitrogen, and may be depleted of oxygen. The methane content may be below, within, or above the flammable or "explosive" range, and, in the case of fire seals, carbon monoxide may be present in concentrations ranging from traces to several percent. Certain of the gases in these atmospheres may be present in percentages beyond the range of equipment suitable for the analysis of air from ventilated places, and, when such is the situation, analytical apparatus designed to accommodate these higher concentrations of gases must be used. Some decrease in accuracy of determination may result from the use of such apparatus, but a high degree of accuracy is not required in analyzing the atmospheres of many unventilated places. For example, if a sealed fire area in a coal mine actually contains 35 percent methane, an error of a few

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9/ American Conference of Governmental Industrial Hygienists, Threshold Limit Values for 1954: Arch. Ind. Hyg. Occup. Med., vol. 9, 1954, pp. 530-534.

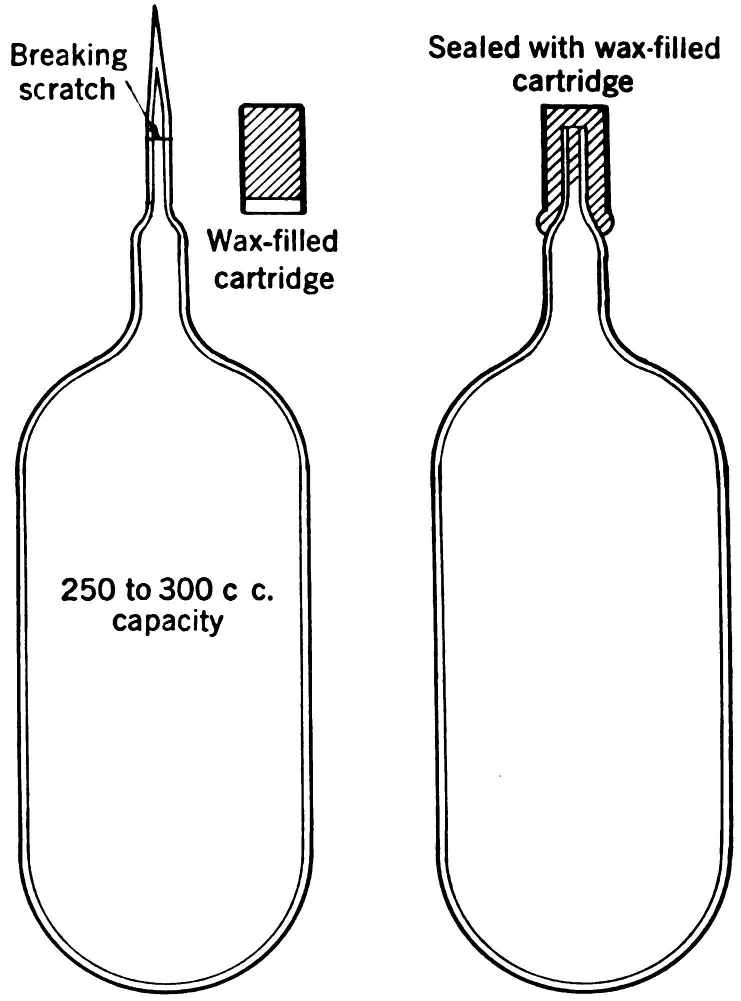


Figure 1. - Vacuum-type sample container.

tenths of a percent or even as much as 1 percent would have no significance or importance in practical interpretation of the analytical results.

One exception to the above statement is in the determination of carbon monoxide in sealed fire areas. When an active fire in a coal mine is first sealed, the carbon monoxide content of the atmosphere in the sealed area may be 1 or 2 percent or more, and extreme accuracy in determination is not necessary, as such concentrations of carbon monoxide may be interpreted only as indicating that the fire still is active. As the fire nears extinguishment and the area cools, the carbon monoxide content will decrease gradually and finally will reach zero if the area is allowed to remain sealed long enough. In such instances it is important to determine mere traces of carbon monoxide, and an analytical method sensitive to at least 0.01 percent of carbon monoxide should be used.

Methods and equipment suitable for the analysis of atmospheres from unventilated places are described in a following section.

The foregoing discussion is intended to show that no one type of equipment or method is applicable to the analysis of all types of mine atmospheres. Suitable analytical results will be obtained only when the equipment or method used is the proper one to fit the existing conditions.

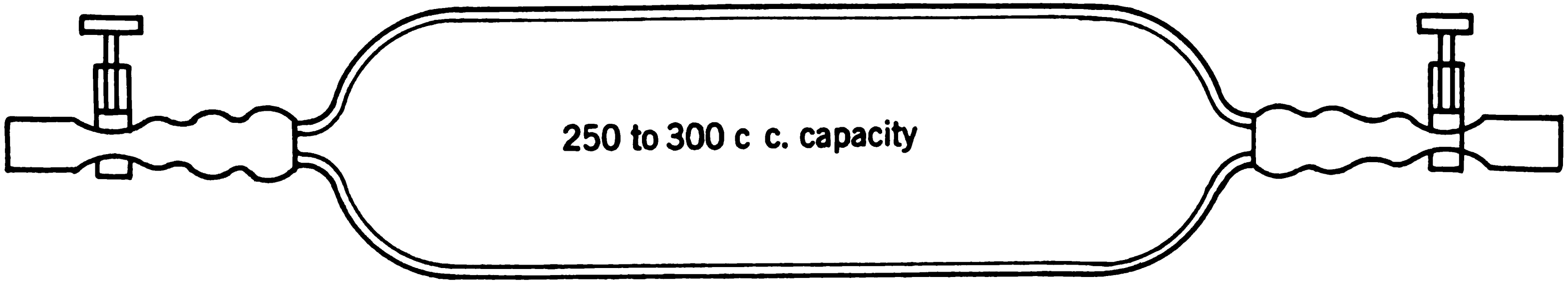
EQUIPMENT FOR SAMPLING MINE ATMOSPHERES

The selection of proper equipment for sampling mine atmospheres is just as important as the choice of analytical methods, because no matter what degree of care and skill may be exercised in the analysis, the results can be no better than the sample. A sample that has been improperly collected, or one whose composition has changed because of faults in the sample container, is worthless, and the results obtained by analysis of such a sample may be seriously misleading. The subject of sampling mine atmospheres is discussed in detail in another Bureau of Mines publication;10/ the following information applies to the various types of containers that may be used in collecting samples of mine atmosphere:

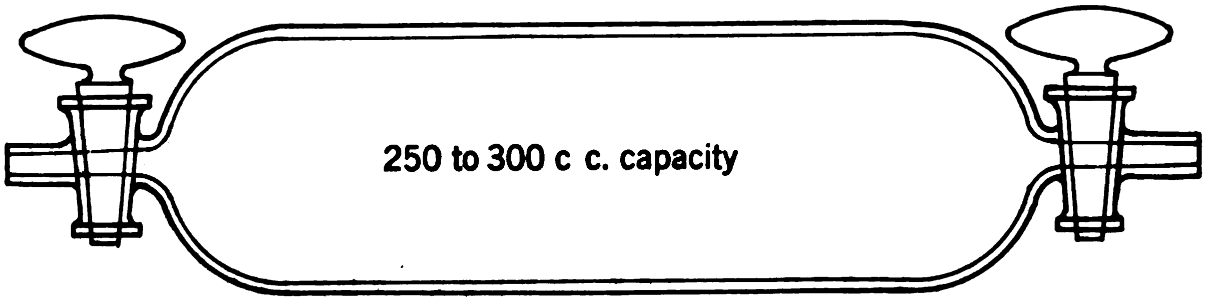
A vacuum-type container (fig. 1) is used almost exclusively by the Bureau of Mines for collecting samples of mine atmosphere, because it has been found most suitable from the standpoints of freedom from leakage, ease of transportation underground, and durability in shipment. After the sample has been withdrawn from this type of container and the analysis has been completed, the opened container is sent to a glass blower for cleaning, repair, reevacuation, and resealing. Use of this type container is practicable only where the necessary facilities for glass blowing and reevacuation can be arranged for, as the cost of a new container for each sample collected would be unreasonably high.

Other types of glass sample containers are shown in figure 2, one type being closed by rubber-tubing connections clamped shut by screw clamps, and the other type being fitted with glass stopcocks. Such containers are rather vulnerable to breakage, and the type fitted with rubber-tubing closures should be used only when the samples will be analyzed soon after collection as gas may diffuse through the rubber and be lost if several days elapse between sampling and analysis.

10/ Berger, L. B., and Schrenk, H. H., Sampling and Analysis of Mine Atmospheres: Bureau of Mines Miners' Circ. 34, 1948 (rev.), 103 pp.



Type A



Type B

Figure 2. - Gas- or liquid-displacement type sample container.

Metal containers of the same general design as those shown in figure 2 may be used and are more durable than the glass containers. The metal stopcocks are more likely to leak than glass cocks, but if inspected and greased frequently will serve satisfactorily. The metal containers should be of brass, zinc, or other nonferrous metal. Iron containers are likely to remove oxygen from the sample through rusting of the interior of the container, and water must be used[11] to displace sample from the metal-type container, and some carbon dioxide is likely to be dissolved from the sample.

Some mining companies use rubber bags as containers for samples of mine atmosphere, inflating the bags and clamping off the inlets at the desired sampling locations. The bags are reported to be satisfactory for sampling atmospheres that are essentially normal air containing small percentages of methane or carbon dioxide. It seems possible, however, that if atmospheres containing high percentages of methane or carbon dioxide were sampled in this manner, some loss of these gases might occur unless the samples were analyzed soon after collection.

Bottles of the type used by druggists for magnesium citrate solution may be used as sample containers. This type of bottle is fitted with a glass stopper seating on a rubber gasket or washer and held in place by a strong spring clamp. The rubber gaskets must be in good condition to insure a gas-tight seal.

Specially prepared evacuated glass containers, as shown in figure 3, are used to collect samples for determining oxides of nitrogen. A small volume of liquid absorbent for oxides of nitrogen is placed in the container before it is evacuated and sealed. Preparation of these containers is described in detail in a Bureau of Mines publication.[12] A sample collected in this type of container may be analyzed only for oxides of nitrogen; if it is desired to determine other constituents of the atmosphere at the same location, an additional sample must be collected in one of the conventional containers.

The selection of sample containers depends on the type of analyses to be made, the method of transportation of samples between mine and laboratory, the time that may elapse between sampling and analysis, and, in the case of the vacuum-type containers, the availability of facilities for evacuating and sealing the containers.

RECORDING OF DATA

In a laboratory where samples of mine atmosphere are to be analyzed as a continuous operation, a systematic procedure should be adopted for identifying the samples and recording this information and the analytical results. A suggestion along this line is shown in figure 4 (top). The required information may be inserted on the label by the collector of the sample at the time of sampling. The collector also fills in the required information on the card shown in figure 4 (bottom), which accompanies the sample container to the laboratory.

When the sample container and card are received at the laboratory, a serial number may be stamped on the card and also on a form for recording the analytical data (fig. 5). This serial number thereafter identifies the sample and the results

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[11] If mercury is used as the displacing liquid, metal sample containers will be damaged by amalgamation.

[12] Beatty, R. L., Berger, L. B., and Schrenk, H. H., Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method: Bureau of Mines Rept. of Investigations 3687, 1943, 17 pp.

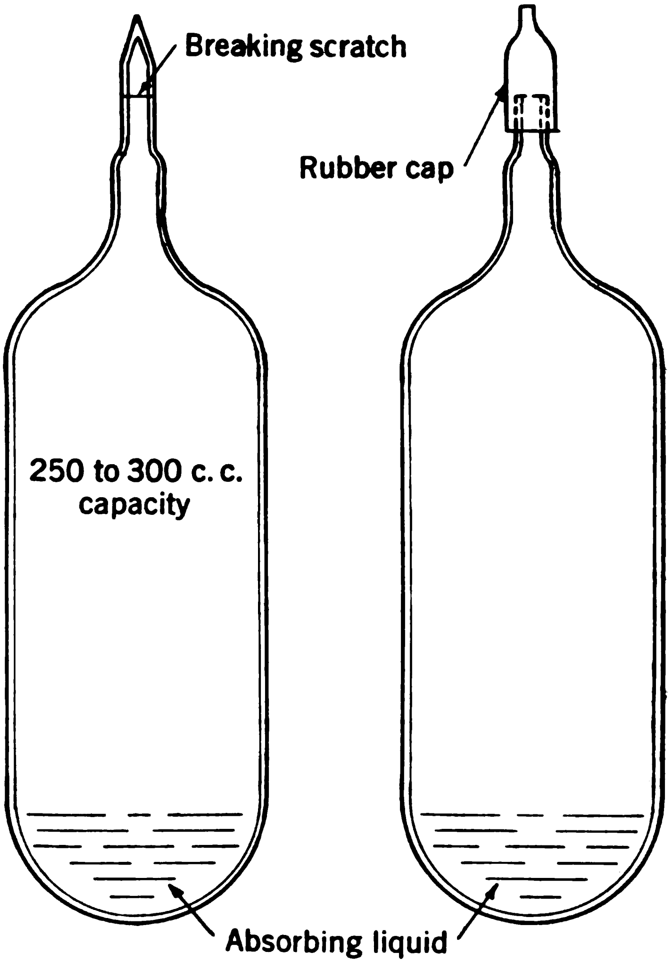

Figure 3. - Special evacuated container for sampling for oxides of nitrogen.

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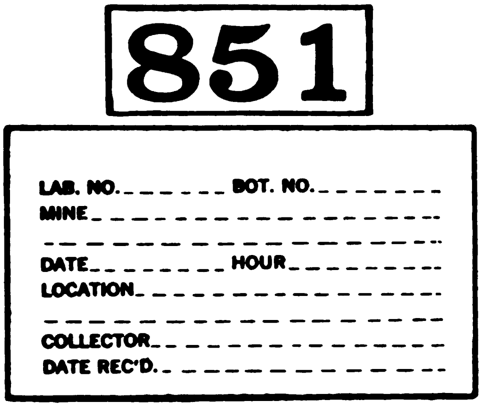

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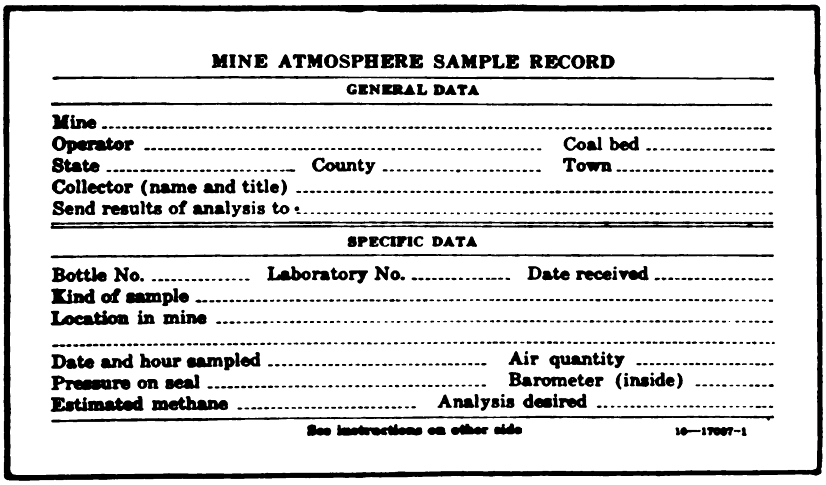
LAB. NO.______ BOT. NO.________
MINE__________________
____
DATE________ HOUR_________
LOCATION________________
____
COLLECTOR_______________
DATE REC'D.______________

Figure 4. - Label and number on vacuum-type sample container.



MINE ATMOSPHERE SAMPLE RECORD

GENERAL DATA

Mine ....
Operator .... Coal bed ....
State .... County .... Town ....
Collector (name and title) ....
Send results of analysis to ....

SPECIFIC DATA

Bottle No. .... Laboratory No. .... Date received ....
Kind of sample ....
Location in mine ....
....
Date and hour sampled .... Air quantity ....
Pressure on seal .... Barometer (inside) ....
Estimated methane .... Analysis desired ....

See instructions on other side 10—17007-1

Figure 4a. - Mine atmosphere sample record that accompanies sample container.

	BURETTE READING	COR-RECTED READING	DIFFER-ENCE	PER-CENT	BURETTE READING	COR-RECTED READING	DIFFER-ENCE	PER-CENT	BURETTE READING	COR-RECTED READING	DIFFER-ENCE	PER-CENT
Volume of sample taken												
Carbon dioxide												
Unsaturated hydrocarbons												
Oxygen												
Hydrogen by CuO at 300° C												
Carbon monoxide by CuO at 300° C												
Oxygen (or air) added												
Total volume												
Volume after burning												
Volume after CO_2 absorption												
Volume after second burning												
Volume after second CO_2 absorption												
Total contraction												
Total CO_2												
Residual O_2												
Total oxygen												
Methane												
Ethane												
Total paraffins												
Nitrogen												

Apparatus No. ____________ *Date* ____________ *Chemist* ____________

Figure 5. - Form for recording data in the analysis of mine atmospheres.

of its analysis. After the sample has been analyzed and the results have been reported, the data card and the analysis form should be filed. It is preferable to keep all original analytical data on file in the laboratory. Any suitable form may be used in reporting the analytical results so long as the sample is properly identified as to location, date of sampling, etc.

EQUIPMENT AND METHODS FOR THE ANALYSIS OF MINE ATMOSPHERES

Haldane Gas-Analysis Apparatus

The Haldane gas-analysis apparatus used by the Bureau of Mines is patterned after the device developed by Haldane[13] and differs from it only in structural modifications that have been added to facilitate operation and simplify construction.

The apparatus was developed to permit determination of carbon dioxide, combustible gases, and oxygen with a degree of accuracy not attainable with apparatus of the types ordinarily used for the analysis of fuel gases, flue gases, and similar mixtures. The Haldane apparatus is used by the Bureau of Mines chiefly in analyzing air samples collected in coal and metal mines and other underground workings and is applied also in analyzing many other types of gas mixtures when accurate determination of certain constituents is desired.

Accuracy of Haldane Apparatus

The Haldane apparatus is well suited to the routine determination of gaseous constituents normally present in mine atmospheres when due consideration is given to the attainable accuracy of results, the limited volume of sample generally available for analysis, and the time required for analysis. Limitations of application are discussed in a subsequent section. In the routine analysis of mine atmospheres as performed in Bureau of Mines laboratories successive portions of each sample analyzed for carbon dioxide and for a single combustible gas shall agree within 0.02 to 0.03 percent by volume, and, for oxygen, within 0.05 percent by volume. In a majority of cases only two analyses are required to obtain such agreement. Many years of experience have proved these limits of precision to be practicable and readily attainable. The greater tolerance allowed for oxygen results from certain limitations of the oxygen-absorbing reagent over and above the normal experimental variations in measuring gas volumes (burette readings may be made to ± 0.002 ml.).

Since finding 0.25 percent or more of methane may result in the classification of a coal mine as gassy,[14] a study of the accuracy of the Haldane method for determining methane concentrations of this order has been made. Forty-four samples of three test mixtures containing known concentrations of methane in air were analyzed. Table 1 shows the distribution of values obtained experimentally in relation to the true values. The methods of procedure in the study of accuracy are presented in detail in an appendix to this information circular.

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[13] Haldane, J. S., Some Improved Methods of Gas Analysis: Jour. Physiol., vol. 22, 1898, pp. 465-480; A Rapid Method of Estimating Carbon Dioxide in Air: Jour. Hyg., vol. 1, 1901, pp. 109-114; Methods of Air Analysis: Charles Griffin and Co., Ltd., London, 1912. Revised and Reprinted 1918. Reprinted 1920. Revised, in collaboration with J. Ivon Graham, and reprinted in 1935. Foster, C. LeN., and Haldane, J. S., The Investigation of Mine Air: Charles Griffin and Co., Ltd., London, 1905, pp. 100-120.

[14] Federal Coal Mine Safety Act: Title II, July 16, 1952, Public Law 552, 82d Congress.

TABLE 1. - Summary of study of accuracy of determination of methane with Haldane-type apparatus

	Single methane determination		Average of two methane determinations on same apparatus		Average of 4 methane determinations--2 on each of 2 different apparatus		Average of 6 methane determinations--2 on each of 3 different apparatus	
	Number	Percent of total	Number	Percent of total	Number	Percent of total	Number	Percent of total
True value plus 0.03 percent	3	1.1	2	1.5	0	0	0	0
True value plus 0.02 percent	3	1.1	2	1.5	0	0	0	0
True value plus 0.01 percent	37	14.1	20	15.3	15	11.5	2	4.7
True value	112	42.8	68	52.0	84	64.6	32	74.4
True value minus 0.01 percent	92	35.1	37	28.2	30	23.1	9	20.9
True value minus 0.02 percent	13	5.0	2	1.5	1	0.8	0	0
True value minus 0.03 percent	2	0.8	0	0	0	0	0	0
Total	262	100.0	131	100.0	130	100.0	43	100.0

The deviation of a single determination of methane was no greater than ±0.03 percent, by volume, from the true value. The maximum deviation of the methane value derived by averaging 2 analyses on an individual Haldane apparatus ranged from +0.03 to -0.02 percent, by volume, from the true value. The maximum deviations of the methane values obtained by averaging 4 determinations (2 each on 2 individual apparatus) were +0.01 and -0.02 percent, by volume, from the true value. The methane value obtained by averaging 6 determinations (2 each on 3 individual apparatus) deviated by no more than ±0.01 percent, by volume, from the true value.

Limitations of the Haldane Apparatus

The Haldane burette, in which gas volumes are measured, is so constructed that the gas mixture undergoing analysis must contain approximately 75 percent of inert gas, such as nitrogen, or a similar percentage of a constituent that is not determined.

In determining combustible gases, the Haldane apparatus is limited to mixtures that do not contain combustibles in sufficient quantity to be flammable and that contain enough oxygen to burn completely all combustible gas present. Gas samples containing combustibles in amounts within or above the flammable limits must be analyzed by other means.

The Haldane apparatus is restricted, therefore, to certain types of gas mixtures, and because of its accuracy and precision is of special value in their analysis.

Principles of Gas-Volumetric Analysis as Applied in the Haldane Apparatus

The analysis of a gas mixture by the gas-volumetric method involves subjecting a measured volume of the mixture to successive treatments, each of which removes a specific constituent of the mixture. Measurement of the decreased volume caused by each such removal permits calculation of the relative proportions of the various constituents in the mixture.

In determining carbon dioxide, combustible gases, and oxygen with the Haldane apparatus this procedure is applied by measuring the gas volumes in a burette, which is essentially a graduated glass tube. Carbon dioxide is removed by passing the gas from the burette into a pipetthat contains an alkaline medium, such as potassium hydroxide solution. Combustible gases are determined by passing the gas sample into a pipet containing an electrically heated platinum wire that causes these gases to burn. Carbon dioxide produced by combustion is removed by again passing the gas into the potassium hydroxide solution. Oxygen is determined by passing the gas into a pipet that contains an oxygen-absorbing medium, such as potassium pyrogallate solution. The gas sample is confined in the burette by a column of mercury, the level of which may be raised and lowered, thus forcing the gas alternately from the burette to the pipets through suitable communicating tubes. Gas volumes measured in the burette are brought to comparable conditions of temperature and pressure by a compensating device attached to the burette.

Factors that May Affect the Accuracy of Analysis

In gas-volumetric analysis certain factors must be considered if results of maximum accuracy are to be obtained. The most important of these, as related to analysis in the Haldane apparatus, are discussed in the following paragraphs.

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Change of Temperature and Barometric Pressure During Analysis

As gas-volumetric analysis consists of a series of measurements of change of volume caused by removal of the various constituents of a mixture, all other factors tending to cause change of volume must be eliminated. The volume of a gas changes with temperature provided the pressure remains constant; therefore, considerable error might be introduced by variations in temperature during analysis unless correction is made for them by calculation, or they are compensated for by the design of the apparatus. Likewise correction or compensation must be made to avoid errors from changes in gas volume owing to variations in barometric pressure during analysis.

The Haldane apparatus is equipped with a device that compensates for changes in temperature or pressure, eliminating the necessity for correcting gas volumes to standard conditions by calculation. All gas volumes measured in the burette are balanced against a fixed volume of gas contained in a closed tube in a water-jacket that also surrounds the burette. Any temperature change that occurs in the apparatus during analysis produces similar effects on the gas in the burette and in the closed compensator tube, and the temperature effect is nullified or cancelled. As the gas volumes measured in the burette are balanced against a fixed volume of gas in the compensator tube, compensation for changes in barometric pressure also is obtained. The use of the compensating device is described in the instructions for operating the apparatus.

Change of Water-Vapor Content of Gas Sample During Analysis

As a volume of gas may contain varying amounts of water vapor, depending upon temperature and degree of saturation of the gas with water vapor, this condition must be controlled in gas-analysis procedures to prevent changes in gas volume by the presence of varying amounts of water vapor during analysis.

In the Haldane apparatus the gas is kept saturated with water vapor by maintaining a small amount of water in the burette at all times. If this procedure were not followed, a sample of dry or incompletely saturated gas, passed into the potassium hydroxide solution for determining carbon dioxide, would gain water vapor from the solution, and the determination would be in error by the amount of water vapor gained. A small amount of water also is maintained in the closed compensator tube, and the effect of variation in vapor-pressure of the water caused by temperature changes is nullified, as the gas in both burette and compensator tube is affected to the same extent.

Solubility of Gases in Confining Liquids

All gases are soluble to some extent in water, and if water were used as the confining liquid considerable error would be introduced through solubility. To eliminate this source of error mercury is used as the confining liquid in the burette and combustion pipet and for displacing gas from the sample container into the burette.

Solubility of Gases in Reagents

In the use of reagents such as potassium hydroxide and potassium pyrogallate solutions, physical solution of some of the constituents of the gas sample is possible, in addition to removal by chemical action of the constituent for which the reagent is specifically intended. Potassium hydroxide solution exerts no significant

solvent action on gases, such as oxygen, nitrogen, methane, carbon monoxide, and hydrogen, that may come into contact with it during the determination of carbon dioxide, and after one or two analyses are made the solubility error becomes negligible. In the case of potassium pyrogallate solution, however, there is appreciable solubility of nitrogen until the reagent has become saturated with that gas. When a fresh solution of potassium pyrogallate is used in the apparatus at least two analyses of normal air should be made before the oxygen values obtained are taken as correct. When gases and vapors such as unsaturated hydrocarbons, gasoline, and benzol are determined in the Haldane apparatus, appreciable solution of these compounds may occur if the sample is passed into the potassium hydroxide solution before combustion. In such instances a modified procedure, described later, usually will eliminate this error.

Calibration of the Burette

Burettes usually are graduated as accurately as possible by the manufacturer, but it is difficult to obtain absolute accuracy over the entire length of a burette of the small diameter used in the Haldane apparatus. Consequently, it is advisable to calibrate the burette before use. The procedure for calibrating burettes is included under Comments on Use and Maintenance of the Apparatus.

Description of Apparatus

Essential parts of the Haldane apparatus are shown in figure 6.

Burette

Burette f (See fig. 6) has a total capacity of 21 ml. The bulb at the upper part of the burette has a capacity of 15 ml. and is not divided by graduations. The capacity of the stem below the bulb is 6 ml., graduated in hundredths of a milliliter. Graduation of the burette begins at the bottom of parallel-bore stopcock e. This stopcock may be turned to communicate through stopcock d and capillary glass tubing c to the sample container, a, or may be rotated from this position through 180 degrees to communicate with the pipets, l, m, and n, through the capillary glass manifold and stopcocks i, j, and k. The burette is enclosed in a water jacket, g, to protect it from sudden temperature changes. A tube connected to a compressed-air supply extends nearly to the bottom of the water jacket, and a stream of air bubbles escaping from this tube produces circulation and uniformity of temperature of the water throughout the jacket. The lower end of the burette is connected by heavy-walled rubber tubing to a leveling bulb, s, which rests in a movable support, t.

Air-Lift for Mercury in Burette

The tedium of repeated manual raising and lowering of the leveling bulb, s, required to pass the gas sample into and to withdraw it from the various pipets, l, m, and n, may be relieved considerably by use of the air-lift device[15] shown in figure 6.

Compressed air at 6 to 6.5 pounds p.s.i.g. may be admitted through a specially designed brass stopcock to a flexible rubber or plastic tube communicating with and fitting tightly into the upper opening of the leveling bulb, s. When gas sample is passed into a pipet, the leveling bulb, s, is raised approximately to the position shown in figure 6 and until the mercury level in the burette, f, is approximately

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[15] Designed by Albert Rhode, of the Gas Analysis Laboratory, Branch of Health Research, Bureau of Mines, Pittsburgh, Pa.

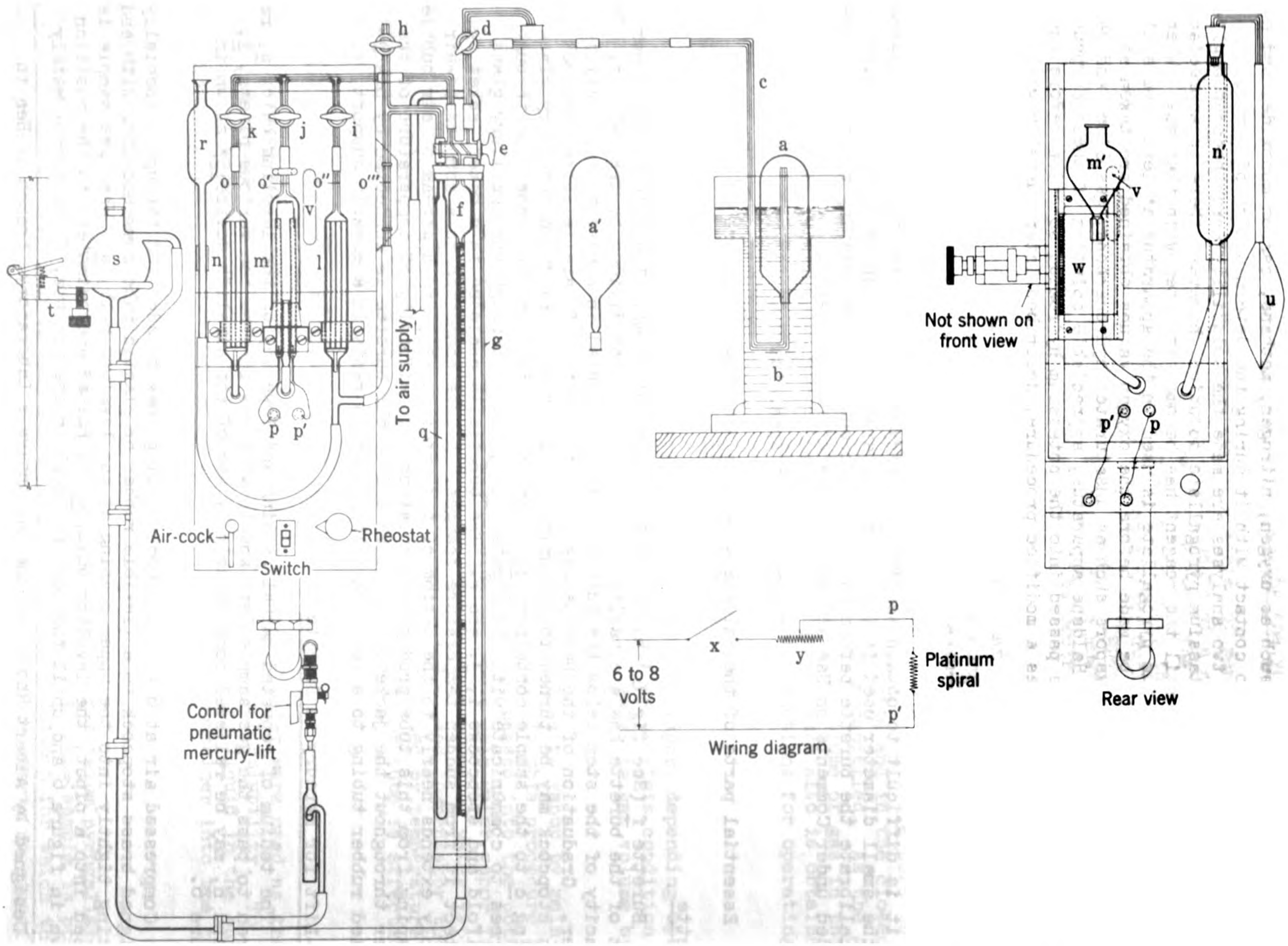

Figure 6. - Diagrammatic sketch of Bureau of Mines Haldane gas-analysis apparatus.

at 15.4 ml., the brass control stopcock is opened applying air pressure to the mercury in s, forcing it downward, and causing the mercury in the burette, f, to rise and fill the bulb at the top of the burette, thus forcing the gas sample into the pipet in use. When the desired limit of motion of the mercury has been reached, the brass stopcock is turned through 90 degrees, closing off the compressed air supply and allowing the air compressed in the leveling bulb, s, and the flexible tubing to escape to the atmosphere through a passageway drilled in the brass control stopcock in such manner that the plug of the stopcock is converted to a T-bore. This procedure allows the mercury in the bulb of the burette to descend to its original level and withdraw most of the gas sample from the pipet. Thus, the gas sample may be passed back and forth repeatedly between the burette and any one of the pipets merely by turning the handle of the brass control stopcock back and forth through 90 degrees.

The analyst can return to manual operation of the leveling bulb, s, as for final manipulation of reagents in the pipets or for making fine adjustments, at any time throughout the analytical procedure by placing the brass control stopcock in the closed position.

Pipets

Pipet l is for the potassium hydroxide solution used in determining carbon dioxide. The lower outlet of this pipet communicates through rubber tubing connections with reservoir r and capillary glass tube o''', which is part of the compensating device. Reservoir r is adjustable vertically.

Combustion pipet m contains a spiral of No. 26 or 28 B. & S. gage platinum wire, which is heated electrically to burn combustible gases. Mercury is used as the confining liquid in this pipet. Two glass tubes support the spiral and are filled with mercury to serve as conductors for the electric current. The upper ends of these tubes are open, and each tube has a short stud of No. 20 B. & S. gage platinum wire sealed to the glass in a vertical position at the opening. These studs furnish electrical contact between the mercury and the spiral, which is held in place by winding its ends around the studs. The lower ends of the tubes are sealed closed around two short lengths of No. 20 B. & S. gage platinum wire, to which are attached wires p and p' connecting to the electrical supply.

Pipet m is connected by rubber tubing to reservoir m', which is mounted on a slide movable vertically by a rack and pinion gear, w, attached to the reverse side of the apparatus. Reservoir m' is mounted in this manner so that it may be lowered and raised as gas is passed into and withdrawn from pipet m, keeping the mercury at approximately the same levels in m and m', thus maintaining the gas in m at approximately atmospheric pressure, thereby reducing the possibility of leakage owing to excessive pressures on the rubber tubing. The level of the mercury in reservoir m' may be observed through slot v in the panel on which the apparatus is mounted.

Pipet n contains the potassium pyrogallate solution used in determining oxygen. The lower outlet of this pipet is connected to reservoir n', the top outlet of which is connected to a rubber bag, u, that protects the reagent from the oxygen of the air.

Pipets l and n contain a number of lengths of small-diameter shell tubing, which, when gas is passed into the pipets, presents a considerable surface wet with reagent, accelerating absorption of gas. The tubes are supported at their lower ends by a helix of glass rod perpendicular to the longitudinal axes of the tubes.

Compensator

Closed tube q of the compensating device is shown in the water jacket, g. The upper end of this tube is connected through capillary glass tubing to tube o'''. Stopcock h is used to bring the pressure in the closed tube to atmospheric before beginning an analysis.

Connections to Gas Sample

The gas sample bottle, a, shown in mercury jar b, is the vacuum type used by the Bureau of Mines in sampling mine atmospheres. A sealed sample bottle is shown at a'. With bottles of this type the gas sample is transferred to the burette through U-tube c. If other types of sample bottles are used, for example those having stopcocks at both ends, c may be replaced by a short elbow of capillary glass tubing.

Electrical Accessories

Electrical accessories used in conjunction with the combustion pipet are indicated in the wiring diagram shown in figure 6. A current supply at 6 to 8 volts is necessary. Variable resistance y may be a rheostat of the carbon pile type used for radio-tube filament control, a wire-wound rheostat of sufficient capacity to prevent overheating, or a length of wire having a resistance of 1 to 2 ohms and equipped with a movable contact. Where alternating current is available, a step-down transformer furnishing current at 6 to 8 volts may be used as the power supply. The capacity of the transformer should be at least 150 watts. Where only direct current is available a lamp bank or other suitable resistance may be used. Storage batteries or dry cells may be employed but are not particularly satisfactory, as storage batteries require frequent recharging and dry cells are rapidly depleted at the rate of current consumption required.

Preparation of Solutions

Potassium Hydroxide

The potassium hydroxide solution used for determining carbon dioxide is prepared by dissolving 300 grams of potassium hydroxide in 1,000 ml. of water. Although potassium hydroxide is preferable, a solution of 200 grams of sodium hydroxide in 1,000 ml. of water also can be used. There is greater tendency, however, toward the deposition of bicarbonate with sodium hydroxide than with potassium hydroxide.

Potassium Pyrogallate

The potassium pyrogallate solution used for determination of oxygen is prepared as follows: Dissolve 50 grams of pyrogallic acid in 150 ml. of water and dissolve 1,200 grams of potassium hydroxide in 800 ml. of water. When the potassium hydroxide solution has cooled, measure 250 ml. of the solution into each of a number of bottles of approximately 325 ml. capacity, such as magnesium citrate bottles. Add 45 ml. of the pyrogallic acid solution to each bottle, close immediately, and mix. Several small bottles are preferable to one large one, as only a small portion of the solution is exposed to the oxygen of the air when the bottle is opened, whereas if stored in a single large container all the solution will be exposed each time the container is opened.

Preparation of Apparatus for Use

Assembling Burette

Burette *f* (fig. 6) is filled by adding clean (preferably distilled) mercury through the leveling bulb, *s*, with stopcock *e* open. Mercury is added until, with *s* raised so that the mercury rises to stopcock *e*, only a few milliliters of mercury remain in *s*.

Two or three milliliters of water are added to the compensator tube, *q*, before it is inserted in the water jacket. Tubes *q* and *o'''* are connected by rubber tubing as shown, and the water jacket is filled with water. Stopcock *e* is connected to the manifold and to stopcock *d* and U-tube *c* by rubber tubing.

Making Rubber Tubing Connections

It is important that rubber tubing of the proper type and size be used in making connections between the various parts of the apparatus. Seamless tubing of the pure-gum type is satisfactory, as it adheres to glass, forming a gastight joint. The inside diameter of the tubing should be such that it makes a snug fit with the glass. For example, rubber tubing of 5 mm. inside diameter should be used to join glass tubes of 7 mm. outside diameter. Rubber tubing connections should be 1-1/4 to 1-1/2 inches in length so that the rubber extends 5/8 to 3/4 inch on each side of the junction of the glass tubes. Fitting the rubber tubing over the glass is facilitated by moistening the interior of the rubber and forcing it onto the glass with a reciprocating rotary motion. The ends of the glass tubes should fit closely together to make as nearly as possible a glass-to-glass joint.

Addition of Water to Burette

When the burette has been assembled, 2 or 3 ml. of distilled water are drawn into the burette through *d* and the leveling bulb, *s*, is lowered until the mercury in the burette reaches the 21 ml. mark. Bulb *s* then is raised until mercury is discharged from the outlet of *d*. This procedure leaves a film of water adhering to the inside surface of the burette. As previously discussed, this film of water must be present at all times during analysis to saturate the gas in the burette with water vapor.

Filling Pipets

The rubber tubing connections between pipet *l*, tube *o'''*, and reservoir *r* are installed next. Sulfur-free tubing of 6 to 8 mm. inside diameter is used. Sulfur-free rubber is used, as the action of potassium hydroxide solution on rubber containing sulfur in time will produce a substance that absorbs oxygen, and carbon dioxide determinations will be in error owing to the absorption of oxygen in addition to carbon dioxide.

The pipets, *l*, *m*, and *n*, are connected next to stopcocks *i*, *j*, and *k* by rubber tubing.

Pipet *l* is filled by adding potassium hydroxide solution to reservoir *r*, with the plug of stopcock *i* removed and stopcock *h* open. The position of *r* and the amount of solution added are regulated so that when the level of the solution in *l* rises to point *o''* the bulb of *r* contains only a few milliliters of solution. If an excessive amount of solution is added, *r* may overflow when gas is introduced into pipet l. This precaution applies also to filling reservoirs n' and m'. When l is filled the plug of stopcock i is replaced.

Pipet n is filled by adding potassium pyrogallate to reservoir n' with the plug of stopcock k removed until the solution rises to point o. The plug of stopcock k is replaced and rubber bag u is partly inflated and inserted in the opening of n', as shown.

Combustion pipet m is filled by adding clean (preferably distilled) mercury to reservoir m', with plug of stopcock j removed, until the mercury rises to point o'. The plug of stopcock j is replaced when m is filled. The glass tubes that support the platinum spiral must be filled completely with mercury. This may be accomplished by adjusting the position of m' so the mercury level in m is just at the tops of the glass tubes and then tapping the pipet so that small globules of mercury drop into the tubes until they are filled. An alternate procedure is to remove the rubber stopper (before mercury is added to the pipet) that supports the tubes and to fill them with mercury through a funnel with a small-diameter stem. When the stopper is reinserted in the pipet it should be moistened and pressed firmly into place to insure a gastight fit.

Adjusting Temperature of Platinum Spiral

When m has been filled the electric connections are attached, the mercury level is lowered until the spiral is exposed, and switch x is closed. The temperature of the spiral is adjusted by rheostat y so that the wire is at a bright yellow heat. It is important to heat the spiral to a temperature that will completely burn the combustible gases but not to the extent of fusing the wire. Switch x is opened after the temperature of the spiral has been adjusted properly.

Greasing Stopcocks

All stopcocks are cleaned and greased. Greasing the stopcocks properly is an important part of the analytical procedure. Improper greasing is likely to cause errors in analysis and difficulties in manipulating the apparatus. Stopcock lubricants suitable for use with the Haldane apparatus are available from laboratory supply houses. Usually it is preferable to purchase these ready-made lubricants rather than to undertake the preparation of a suitable lubricant in the laboratory.

The plug and barrel of the stopcock are cleansed by wiping with cheesecloth. The barrel may be cleaned by wrapping two or three layers of cheesecloth over the end of a pencil and passing this through the barrel with a rotary motion. The capillary openings may be cleaned with a pipe cleaner or soft copper wire. Instruments that might scratch the ground surface of the stopcock should not be used. The stopcock is lubricated by placing a thin layer of grease, extending the length of the plug, along the sides of the plug not pierced by the bore. The plug is inserted in the barrel, pressed firmly into place, and rotated several times in both directions. If greased properly, an even, transparent film of grease covers the ground surfaces of the stopcock at all points of contact. Application of the proper amount of grease is a skill learned best by experience. If too little grease is applied, striations and bubbles will be evident, and the stopcock may leak. If an excess of grease is used the bore will become plugged in a short time, impeding or stopping flow of gas through the stopcock. Stopcock plugs often are not interchangeable, and it is best to remove only one plug at a time to avoid confusion.

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Adjusting Levels of Liquids in Pipets

The solutions in pipets *l* and *n* and the mercury in pipet *m* are brought to *o*, and *o''*, by drawing about 20 ml. of air into the burette and turning stopcock *e* to communicate with the manifold. Stopcock *i* is opened and the level of the solution is adjusted to mark *o''* by raising or lowering leveling bulb *s* as necessary. This procedure, from the opening of stopcock *i*, must be conducted with care, as the caustic solution in *l* may easily be drawn into the manifold and possibly into the burette. If this should occur all parts accidentally brought into contact with caustic solution must be cleaned thoroughly with dilute sulfuric acid.

The same procedure is used in bringing the liquids in pipets *n* and *m* to marks *o* and *o'*. The precautions regarding manipulation of the caustic solution apply in adjusting the potassium pyrogallate solution in *n* to mark *o*.

Testing for Leaks

The apparatus is next tested for leaks. Stopcocks *e* and *d* are turned to communicate with the atmosphere, and the leveling-bulb, *s*, is lowered until about 20 ml. of air has been drawn into the burette. Stopcock *e* is then closed, and *s* is raised to the top of its supporting rod. A gradual rise in the level of mercury in the burette indicates a leak at stopcock *e*. If the mercury level remains stationary, turn *e* to communicate with the manifold. A gradual rise in mercury level in the burette indicates leakage at stopcocks *i*, *j*, or *k* or at the rubber tubing connections between *e* and the manifold. Leakage at *i*, *j*, or *k* usually, but not always, causes the solutions to drop from marks *o*, *o'*, and *o''*. If no leaks are indicated, the rubber tubing connections below *i*, *j*, and *k* are tested next. Reservoirs *n'* and *m'* are lowered as far as possible and maintained in that position for several minutes. If no leaks are present in the rubber tubing connections below stopcocks *k* and *j*, the liquids in pipets *n* and *m* will return to marks *o* and *o'* when *n'* and *m'* are returned to their former positions. With stopcock *h* open, reservoir *r* is adjusted so that the solution in the compensator tube coincides with mark *o'''*. (If the level of the solution in *l* does not coincide with *o''* it should be brought to that mark by opening *i*, adjusting the leveling-bulb, *s*, and closing *i*.) Stopcock *h* is closed and *r* lowered as far as possible for several minutes. If a leak exists in the rubber connection below stopcock *i*, the solution will fail to return to *o''* when *r* is returned to its former position; if the solution fails to return to mark *o'''*, a leak exists in *h* or in the rubber connection with closed tube *q*.

Leaks at stopcocks may be corrected by regreasing or, if this fails, by regrinding (see Comments on Use and Maintenance of Apparatus) and regreasing. Leaks at rubber tubing connections may be corrected by replacing the tubing; if the tubing that leaked did not appear to fit tightly to the glass, it should be replaced by tubing of smaller inside diameter, or the joint between glass and rubber may be improved by wrapping the rubber connection, at about one-quarter inch from each end, with two strands of No. 22 copper wire, twisting the free ends of the wire together after wrapping.

Stopcock *d* and rubber connections to U-tube *c* are tested for leaks by turning *d* to communicate with *c*, raising the leveling-bulb, *s*, until the mercury in the burette, *f*, rises to stopcock *e*, closing the outlet of *c* by placing a finger over the open end of the tube, and lowering *s*. If the mercury level in *f* continues to fall, a leak is indicated between *e* and *c*.

Analytical Procedure

Filling Manifold With Nitrogen

After the apparatus has been assembled and tested for leaks, the first step in the analytical procedure is to fill the manifold from stopcock e to marks o, o', and o'' with nitrogen. As the manifold is not purged by the mercury in the burette when a sample is drawn into the apparatus, its volume is "dead space" and must be filled with a gas that is inert with respect to the various treatments to which the gas sample is subjected. To fill the manifold with nitrogen, 20 ml. of air is drawn into the burette through stopcocks e and d; e is turned to communicate with the manifold, stopcock k is opened, and the air sample in the burette, f, is passed back and forth between f and pipet n by raising and lowering the leveling bulb, s. Ten to twelve passes usually are sufficient to absorb the oxygen from the air sample. (As an aid in determining when the oxygen has been absorbed, the color of the potassium pyrogallate solution adhering to the tubes in the pipet may be observed. While oxygen is being absorbed the film of reagent on these tubes becomes brownish-red. When the oxygen has been absorbed the reagent assumes a greenish hue. Four or five additional passes should be made after the red no longer can be observed.) After the oxygen has been absorbed, the residual nitrogen[16] is withdrawn from n to the burette, f, and k is closed. The gas then is passed once into pipets m and l to remove the oxygen present in the capillaries below stopcocks i and j. When the gas is withdrawn from these pipets the liquids in the pipets are adjusted to marks o' and o'', and i and j are closed. The gas is again passed six times into n to remove the oxygen picked up in the capillaries below i and j. When this has been done the gas is returned to f, the liquid in n is brought to mark o, and k is closed.

Stopcocks i and h are opened and the level of the potassium hydroxide solution adjusted to marks o'' and o'''. Stopcocks i and h then are closed, and stopcock e is rotated 180 degrees. This procedure leaves the manifold filled with nitrogen at "compensated pressure" and brings the air in the closed tube of the compensator to atmospheric pressure. Stopcock h must not be opened during an analysis, but may be opened between analyses to reestablish atmospheric pressure in the closed tube of the compensator and should be left open when the apparatus is not in use.

Drawing Sample Into Burette

Stopcocks e and d are turned to communicate with U-tube c, and the leveling bulb, s, is raised until mercury flows from the outlet of c. Stopcock e is then turned 90 degrees.

If the gas to be analyzed is contained in a vacuum-type sample bottle, as shown in figure 6, a file mark is made on the neck of the bottle, the neck is placed under mercury in jar b, and broken off by tapping against the side of the jar. The open end of the sample bottle is kept beneath the mercury, and c is inserted as shown in figure 6. If the sample is contained in a tube having stopcocks at both ends, c is replaced by a short elbow of capillary tubing. One stopcock of the sample tube is attached to the outlet of this elbow by rubber tubing and the other submerged in the mercury in jar b before opening.

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[16] As the potassium pyrogallate solution is alkaline, the carbon dioxide of the air is removed along with the oxygen. The residual nitrogen of the air contains about 1 percent of the "noble gases" (argon, neon, xenon, krypton, and helium), which are inert and which, in ordinary gas analysis, are included in the term "nitrogen."

After the sample tube has been connected s is lowered, e is turned to communicate with the sample, and 18 to 20 ml. of sample is drawn into the burette, f. Stopcock d then is turned to communicate with the atmosphere, and s is raised until mercury flows from the outlet of d to discharge bubbles of air that may have been trapped in the capillary between U-tube c and stopcock e. Stopcock d is turned to communicate with the sample, and s is lowered until approximately 20 ml. of sample has been drawn into f. The position of the sample tube is adjusted so that the levels of the mercury inside and outside the sample tube coincide, and e is turned to communicate with the manifold.

Reading Burette

Stopcock i is opened cautiously (the level of the solution in pipet l should not move very far in either direction from mark o'') and the positions of leveling-bulb s and reservoir r so adjusted that the solution in l is at mark o'' and that in the compensator tube at mark o'''. The volume of gas sample in the burette, f, is then read to the nearest 0.002 ml. (with stopcock i open), which gives the volume of sample taken for analysis.

The "compensating" procedure described in the foregoing paragraph - that is, the adjustment of the level of the potassium hydroxide solution to marks o'' and o''' - is followed throughout the analysis before each volume reading in the burette is made.

Determining Carbon Dioxide

Carbon dioxide is removed from the sample by raising and lowering the leveling-bulb, s, with stopcock i open, causing the gas to pass back and forth between burette f and pipet l. After six passes into l the gas is withdrawn to f, the level of the potassium hydroxide solution adjusted to marks o'' and o''', as previously described, and the burette reading taken. It is well to check this reading, until technique is perfected, by passing the gas into l six more times and again reading the burette. After the burette is read, stopcock i is closed. The burette reading is subtracted from the original volume of sample to obtain the volume of carbon dioxide in the sample. The percentage of carbon dioxide in the sample is calculated as follows:

$$\text{Percent, by volume,}^{[17]} \text{ of carbon dioxide} = \frac{\text{volume of carbon dioxide}}{\text{original volume of sample}} \times 100$$

Determining Combustible Gases

Combustible gases are determined by opening stopcock j and passing the gas into pipet m, lowering reservoir m' at the same time so that the mercury levels in m and m' coincide. When the platinum spiral is exposed, switch x is closed. (The Haldane apparatus is not designed for determining combustible gas-air mixtures within the flammable range. If an attempt is made to burn a flammable mixture in pipet m, an explosion may result. If there is doubt as to the amount of combustible in the sample, a piece of wire screen or shatter-proof glass should be placed in front of the pipet to protect the operator.) To cool the pipet a stream of air is directed over it by a curved glass or metal tube (shown surrounding the capillary outlet of m in fig. 6) pierced on the lower side by a number of small holes. If the temperature of the platinum spiral has not been adjusted previously it should now be adjusted to the proper temperature. (See Preparation of Apparatus for Use.) The gas is passed back and forth between the burette, f, and pipet m 8 to 10 times, keeping the mercury in m and m' at the same level. Switch x is opened, and the pipet is allowed to cool to room temperature. The gas is withdrawn to f, the mercury in m brought to mark o', and stopcock j closed. Stopcock i is opened, the level of the potassium hydroxide solution brought to marks o'' and o''', and the burette reading taken. This reading subtracted from that obtained after removal of the carbon dioxide gives the contraction in volume owing to combustion.

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[17] The results of gas-volumetric analysis are reported as percent by volume rather than percent by weight. The results usually are reported on a dry basis, that is, account is not taken of the water-vapor content of the sample.

Carbon dioxide produced by combustion is determined by passing the gas six times into l, compensating, and reading the burette. If the contraction owing to combustion exceeds 0.200 ml., the sample should be subjected to combustion a second time and the carbon dioxide produced by the second combustion determined. The two contractions and the two carbon dioxide values are added to obtain the total contraction in volume and the total carbon dioxide produced by combustion. If methane is the only combustible gas in the sample, the percentage of methane is calculated from these values as follows:

$$\text{Volume of methane in sample} = \frac{\text{contraction caused by combustion} + \text{carbon dioxide formed}}{3}$$

$$\text{Percent, by volume, of methane} = \frac{\text{volume of methane}}{\text{original volume of sample}} \times 100$$

Methods for calculating the volumes of combustible gases other than methane and of various combinations of combustible gases are given in the section on Calculating Results.

Determining Oxygen

Oxygen is removed from the sample by passing the gas into the potassium pyrogallate solution in pipet n. The gas is passed 12 times (this number of passes usually suffices but it is advisable to observe the color change in the solution, as previously mentioned) into pipet n and then is withdrawn to the burette, f, stopcock k is closed, and the gas is passed once into pipets m and l to pick up oxygen remaining in the capillaries below stopcocks j and i. The gas is then passed six times more into n and withdrawn to f, the level of the solution in n being adjusted to mark o before k is closed. The volume of gas in the burette is compensated and the burette reading taken. It is well to check this reading by passing the gas again into n four or five times and taking a second burette reading. This reading, subtracted from the reading obtained after the final removal of carbon dioxide produced by combustion, gives the volume of oxygen remaining in the sample after combustion. If the sample contains combustible gas, a definite volume of oxygen has been consumed in the combustion, and this volume of oxygen must be calculated and added to the volume of oxygen determined by absorption to obtain the total volume of oxygen in the sample.

If methane is the only combustible gas in the sample the calculation is as follows:

Volume of oxygen consumed in combustion = 2 x volume of methane.

Total volume of oxygen in sample = volume of oxygen determined by absorption + volume of oxygen consumed in combustion.

$$\text{Percent, by volume, of oxygen} = \frac{\text{total volume of oxygen}}{\text{original volume of sample}} \times 100$$

Calculation of oxygen consumed in combustion of various gases is illustrated in the section on Calculating Results.

Determining Nitrogen

The percentage of nitrogen is obtained by subtracting the sum of the percentages of the other constituents from 100:

Percent, by volume, of nitrogen = 100 - (percent carbon dioxide + percent combustible gas + percent oxygen).

Calculating Results

In the preceding section, Analytical Procedure, the volume of methane in the sample was calculated by adding the contraction in volume and the carbon dioxide produced by combustion and dividing this sum by three. This calculation is based on the volume relations expressed by the reaction

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

One volume[18] of methane requires 2 volumes of oxygen for complete combustion, and 1 volume of carbon dioxide and 2 volumes of water vapor are formed. As the water vapor condenses and occupies negligible space, the carbon dioxide is the only measurable product of combustion. Therefore, 3 volumes of gas are reduced to 1 volume by combustion. In other words, the contraction produced by combustion of 1 volume of methane is twice the volume of the methane, and the carbon dioxide produced is equal to the volume of the methane, as shown in the following equations:

$$\text{Contraction} = 2 \times CH_4$$

$$\text{Carbon dioxide} = CH_4$$

Combining and solving these equations,

$$\text{Methane} = \frac{\text{contraction} + CO_2}{3}$$

Formulas for calculating the volume of any single combustible gas may be derived in the same manner. For example, from the reaction

$$2\ CO + O_2 = 2\ CO_2$$

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[18] The term "volume" means any unit volume, as milliliter, cubic inch, cubic foot, etc.

$$\text{Carbon monoxide}^{19/} = 2/3\ (\text{contraction} + CO_2)$$

and from the reaction.

$$2\ H_2 + O_2 = 2\ H_2O$$

$$\text{Hydrogen} = 2/3\ \text{contraction}$$

These reactions indicate also that carbon monoxide and hydrogen require one-half their volume of oxygen for complete combustion.

The following example illustrates data relating to analysis of a sample of coal-mine air containing carbon dioxide, methane, oxygen, and nitrogen.

Analytical Data

	Burette reading, ml.	Difference, ml.
Volume of sample taken for analysis	20.010	
Volume after carbon dioxide absorption	19.978	
Contraction owing to carbon dioxide absorption		0.032
Volume after combustion	19.922	
Contraction owing to combustion		.056
Volume after carbon dioxide absorption	19.894	
Carbon dioxide owing to combustion		.028
Volume after absorption of residual oxygen	15.820	
Residual oxygen		4.074
Oxygen consumed in combustion of methane		.056
Total oxygen		4.130

Calculations

	Percent by volume
Carbon dioxide $\frac{0.032}{20.010} \times 100$	0.16

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[19] If a sample is suspected of containing carbon monoxide in amounts at, or near, the limit of accuracy of the Haldane apparatus, the gas-volumetric analysis should be supplemented by tests specific for carbon monoxide, such as the pyrotannic acid method, to verify the presence or absence of this gas. See Sayers, R. R., and Yant, W. P., The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and in Air: Tech. Paper 373, Bureau of Mines, 1925, 18 pp.

When carbon monoxide is known to be present, concentrations of 0.1 percent or more may be determined with a modification of the Haldane-type apparatus. See Berger, L. B., Determination of Carbon Monoxide by Absorption in the Haldane-Type Gas Analysis Apparatus: Bureau of Mines Rept. of Investigations 4187, 1947, 6 pp.

Concentrations of carbon monoxide less than 0.1 percent may be determined colorimetrically by use of a special reagent. See Polis, B. D., Berger, L. B., and Schrenk, H. H., Colorimetric Determination of Low Concentrations of Carbon Monoxide by Use of a Palladium Chloride-Phosphomolybdic Acid-Acetone Reagent: Bureau of Mines Rept. of Investigations 3785, 1944, 13 pp.

Calculations (Con.)

	Percent by volume
Methane $\frac{0.056 + 0.028}{3} = 0.028$	
$\frac{0.028}{20.010} \times 100$	0.14
Oxygen $(2 \times 0.028) + 4.074 = 4.130$	
$\frac{4.130}{20.010} \times 100$	20.64
Nitrogen (by difference) $100 - (0.16 + 0.14 + 20.64)$	79.06

The volume of each gas in mixtures containing any two of the gases methane, carbon monoxide, and hydrogen may be calculated from contraction and carbon dioxide produced by combustion. The calculations are based on the following reactions:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O \qquad (1)$$

$$2\ CO + O_2 = 2\ CO_2 \qquad (2)$$

$$2\ H_2 + O_2 = 2\ H_2O \qquad (3)$$

Methane and carbon monoxide. - When the mixture contains methane and carbon monoxide the following relations are obtained from equations (1) and (2):

$$\text{Contraction} = 2 \times CH_4 + 1/2\ CO \qquad (4)$$

$$\text{Carbon dioxide} = CH_4 + CO \qquad (5)$$

Solving equations (4) and (5),

$$\text{Methane} = \frac{2 \times \text{contraction} - CO_2}{3}$$

$$\text{Carbon monoxide} = CO_2 - CH_4$$

Methane and hydrogen. - When the mixture contains methane and hydrogen the following relations are obtained in like manner from equations (1) and (3):

$$\text{Methane} = CO_2$$

$$\text{Hydrogen} = \frac{2 \times \text{contraction} - 4 \times CO_2}{3}$$

Hydrogen and carbon monoxide. - When the mixture contains hydrogen and carbon monoxide the following relations are obtained from equations (2) and (3):

$$\text{Hydrogen} = \frac{2 \times \text{contraction} - CO_2}{3}$$

$$\text{Carbon monoxide} = CO_2$$

Methane, carbon monoxide, and hydrogen. - When the mixture contains methane, carbon monoxide, and hydrogen, the volume of oxygen consumed by combustion must be determined in addition to the contraction and carbon dioxide produced by combustion to calculate the volume of each gas. The volume of oxygen consumed is determined by subjecting one portion of the sample to the complete procedure - determining carbon dioxide, contraction owing to combustion, carbon dioxide produced by combustion, and residual oxygen remaining after combustion - and analyzing a second portion of the sample for carbon dioxide and oxygen only. The oxygen consumed by combustion in the first portion is calculated as follows:

First portion (A). - Carbon dioxide, contraction and carbon dioxide produced by combustion and residual oxygen determined.

Second portion (B). - Carbon dioxide and oxygen determined.

$$\text{Percent oxygen in B} = \frac{\text{volume of oxygen determined}}{\text{original volume of sample}} \times 100$$

$$\text{Total volume oxygen in A} = \frac{\text{original volume of A} \times \text{percent oxygen in B}}{100}$$

Volume oxygen consumed in combustion of A = total volume oxygen in A - volume residual oxygen in A.

From equations (1), (2), and (3), the following relations are obtained:

$$\text{Hydrogen} = \text{contraction} - \text{oxygen consumed},$$

$$\text{Methane} = \frac{(2 \times \text{contraction} - CO_2)}{3} - H_2$$

$$\text{Carbon monoxide} = CO_2 - CH_4$$

When two or more gases are determined by combustion the small, unavoidable errors of analysis may be cumulative in random instances and in such instances may be multiplied in the calculations, reducing to some extent the accuracy and precision of determinations of these gases.

A typical analysis of a sample containing carbon dioxide, hydrogen, methane, carbon monoxide, oxygen, and nitrogen follows:

First portion. -

	Burette reading, ml.	Difference, ml.
Volume of sample taken for analysis	20.430	
Volume after carbon dioxide absorption	20.185	
Contraction owing to carbon dioxide absorption		0.245
Volume after combustion	20.002	
Contraction owing to combustion		.183
Volume after carbon dioxide absorption	19.882	
Carbon dioxide owing to combustion		.120
Volume after oxygen absorption	16.180	
Residual oxygen		3.702

Second portion. -

	Burette reading, ml.	Difference, ml.
Volume of sample taken for analysis	20.270	
Volume after carbon dioxide absorption	20.025	
Contraction owing to carbon dioxide		.245
Volume after oxygen absorption	16.205	
Contraction owing to oxygen absorption		3.820

Calculations.- From analysis of the second portion the oxygen content of the sample is $\frac{3.820}{20.270} \times 100$, or 18.85 percent by volume.

Total volume of oxygen in first portion =

$$\frac{20.430 \times 18.85}{100} = 3.851 \text{ ml.}$$

Volume oxygen consumed in combustion of first portion =
3.851 - 3.702 (residual oxygen of first portion) = 0.149 ml.

Volume hydrogen in first portion = contraction - oxygen consumed =
0.183 - 0.149 = 0.034 ml.

Volume methane in first portion = $\frac{2 \times \text{contraction} - CO_2}{3} - H_2 =$

$$\frac{0.366 - 0.120}{3} - 0.034 = 0.048 \text{ ml.}$$

Volume carbon monoxide in first portion = $CO_2 - CH_4 = 0.120 - 0.048 =$
0.072 ml.

Results of analysis. -

	Percent by volume
Oxygen = $\frac{3.820}{20.270} \times 100$ (from analysis of second portion) =	18.85
Carbon dioxide = $\frac{0.245}{20.430} \times 100$ (from analysis first portion) =	1.20

Results of analysis (Con.)

	Percent by volume
Hydrogen $= \frac{0.034}{20.430} \times 100$ (from analysis first portion) =	0.17
Methane $= \frac{0.048}{20.430} \times 100$ (from analysis first portion) =	.23
Carbon monoxide $= \frac{0.072}{20.430} \times 100$ (from analysis first portion) =	.35
Nitrogen (by difference) $= 100 - (18.85 + 1.20 + 0.17 + 0.23 + 0.35) =$	79.20

Hydrocarbon-air mixtures. - Saturated hydrocarbons of the formula C_nH_{2n+2}, such as natural gas and gasoline vapor, may be calculated from the following equation:

$$\text{Volume of hydrocarbons} = \frac{2 \times \text{contraction} - CO_2}{3}$$

If the combustible consists mainly of higher hydrocarbons, as "wet" natural gas or gasoline vapor, it is advisable to determine only contraction and carbon dioxide produced by combustion, as these higher hydrocarbons are appreciably soluble in the potassium hydroxide solution, and if the sample is passed first into this solution to determine carbon dioxide, error may be introduced through solubility. If the sample consists of hydrocarbons and normal air, correction may be applied to the combustion data for the carbon dioxide content of the air (0.03 percent).

Comments on Use and Maintenance of Haldane Apparatus

Location of Apparatus

The Haldane apparatus should be installed in a location free from drafts and not subject to wide variations or sudden changes in temperature. Sudden changes in temperature during an analysis may cause the level of the liquid in the compensating tube to move beyond the working range of the apparatus.

Calibration of Burette

The burette is calibrated while in the water jacket, which is filled with water and maintained at as nearly constant temperature as possible. A thermometer inserted in the water jacket indicates the temperature. A two-way stopcock is sealed to the lower end of the burette, mercury is introduced into the burette through a leveling-bulb and rubber tubing attached to one outlet of this stopcock, and mercury is added until it reaches the bottom of the stopcock at the upper end of the burette. Successive portions of mercury are withdrawn through the open outlet of the lower stopcock and weighed. The burette reading is noted after each portion is withdrawn. The true volume of each portion is calculated from its weight and observed temperature.

Precautions Against Contamination of Apparatus by Caustic Solutions

It is of utmost importance to keep the stopcocks, manifold, combustion pipet, and burette free of the slightest traces of potassium hydroxide or potassium pyrogallate solutions if accurate analyses are to be obtained. Even though the solutions have not been observed to enter these parts of the apparatus, it is advisable to cleanse them if the results of analysis seem doubtful and no other cause of error is evident. The mercury used in displacing the sample from its container and all connections to the sample container also must be kept free of caustic.

Cleaning Manifold

The preferred method of cleaning the manifold is to remove it from the apparatus and draw through it, in the order named, dilute sulfuric acid, distilled water, and air.

Cleaning Burette

The burette may be cleaned by a mixture of equal parts of concentrated sulfuric acid and saturated potassium dichromate solution. An alternate procedure is to draw into the burette a solution of 90 percent concentrated nitric acid and 10 percent water, allow it to remain for a few minutes, and then discharge it. A solution containing 50 percent concentrated nitric acid is used next, followed by solutions containing 25 and 5 percent concentrated nitric acid, and finally the burette is washed several times with distilled water. This may be done without draining the mercury from the system, as the gradual decrease in acid concentration prevents deposition of mercurous nitrate on the walls of the burette.

Organic solvents should not be used to clean any part of the apparatus.

Grinding Stopcocks

If stopcocks are unsatisfactory owing to poor fit between plug and barrel or if they become eroded by wear or the action of caustic solutions, they may be reground by the following procedure: The plug of the stopcock is given a thin coating of moistened abrasive (400 to 600-mesh), inserted in the barrel lightly, and turned with a reciprocating rotary motion. The plug is withdrawn from the barrel after each four or five turns to prevent formation of grooves in the ground surfaces. At intervals the stopcock is washed free of abrasive, dried, and greased. When an even, transparent film of grease is obtained between plug and barrel at all points of contact, grinding is complete. (If the stopcock is deeply eroded, so much grinding may be necessary that the capillary bores are thrown out of alinement and the stopcock becomes useless.)

Analysis of Normal Air to Check Analytical Procedure

Technique of operation and condition of apparatus may be considered satisfactory when the results obtained in analysis of normal air are in agreement with its actual composition (0.03 percent carbon dioxide, 20.95 percent oxygen, 0.00 percent combustible, and 79.02 percent nitrogen).

Difficulties Encountered in Using Haldane Apparatus

In the use of the Haldane apparatus, as with any analytical procedure, difficulties may be encountered, and their sources are determined most readily by systematic consideration of their possible causes. The difficulties most likely to be encountered in the use of the Haldane apparatus, and their possible causes are:

Difficulty encountered	Possible causes
Leaks in apparatus:	Defective or deteriorated rubber tubing; tubing of improper size; improperly greased or poorly fitting stopcocks; defects in glassware; rubber stopper at base of combustion pipet improperly fitted; faulty glass-platinum seal in combustion pipet electrodes.
Expansion in volume when carbon dioxide is determined:	Leaks; insufficient water in burette to maintain sample in saturated condition.
Incorrect value for oxygen percentage in analysis of normal air:	Leaks; insufficient water in burette; potassium pyrogallate solution exhausted; absorption of nitrogen by fresh potassium pyrogallate solution; oxygen not completely absorbed; burette dirty or improperly calibrated.
Repeat burette readings do not agree in determination of a particular constituent:	Leaks; solutions exhausted; constituent not completely absorbed; in determination of combustibles, temperature of platinum spiral may be too low.
Expansion in volume after combustion:	Leaks; sample does not contain enough oxygen for complete combustion of combustibles.
Inexactness in combustion data: For example, methane is known to be the only combustible gas present, but ratio of contraction to carbon dioxide produced is not 2 to 1[20]	Leaks; insufficient water in burette; potassium hydroxide or potassium pyrogallate solution present in manifold, burette, or combustion pipet.

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[20] Although the theoretical ratio of contraction to carbon dioxide produced in the combustion of methane is 2 to 1, some occasional variation from this ratio may occur when low concentrations of methane are determined because the possible error of burette reading (0.002 ml.) becomes a significant proportion of the observed volumes of contraction and carbon dioxide produced. For example, in the determination of methane in a concentration of 0.25 percent, the possible errors in burette reading may combine in such manner that combustion ratios ranging from 2.26:1 to 1.78:1 are produced. Unless definite reason exists to suspect that combustible gases other than methane may be present, such combustion ratios, in this low order of methane concentration, may be accepted as amenable to calculation in terms of methane, for, although much closer approach to the theoretical combustion ratio for methane is attainable with the Haldane type apparatus, the significance, magnitude, and frequency of occurrence of possible random error must be taken into account, as in considering any type of observed measurement.

Difficulty encountered	Possible causes
Liquid in compensating device appears sluggish in movement	Capillary between burette and potassium hydroxide pipet blocked by globule of water, mercury, or stopcock grease.
Liquids do not remain at marks in capillaries of pipets	Leaks; manifold not filled with inert gas.
Duplicate analyses do not agree within satisfactory limits	Any of the foregoing causes.

List of Equipment for Haldane Apparatus

Many of the items listed in connection with the Haldane apparatus are suitable for use in other gas-analysis procedures. Most of the items may be purchased from laboratory supply houses. Some may be constructed by the prospective user if he so desires.

Apparatus Assembly

The apparatus preferably should be obtained as a complete unit, including the supporting frame, all necessary glass parts, rubber tubing connections, and transformer and rheostat for power supply to combustion pipet. The transformer and rheostat are included in the assembly of some commercial apparatus. With others it may be necessary to purchase transformer and rheostat separately. The capacity of the transformer should be at least 150 watts, the primary should be suitable for use on the voltage and frequency available in the laboratory, and secondary voltage should be 6 to 8. The rheostat should be capable of carrying 2 to 3 amperes without overheating.

Spare Parts

It is good policy to keep on hand a supply of spare glass and electrical parts for the apparatus, as breakage or failure of a single part may make the whole apparatus inoperative. Some No. 28, B. & S.-gage platinum wire should be on hand for replacing burned-out or broken coils in the combustion pipet. Approximately 3 inches of wire are required for 1 coil.

Rubber Tubing

A supply of rubber tubing should be kept on hand, as connections on the apparatus must be replaced from time to time. For most commercial apparatus the following sizes are suitable:

For manifold - 3/16-inch inside diameter, 1/16- or 3/32-inch wall, pure gum.

For lower connection to carbon dioxide pipet - 1/4-inch inside diameter, 3/32-inch wall, pure gum or sulfur-free rubber, or chemical-resistant synthetic.

For leveling bulbs - 3/16-inch inside diameter, 1/8-inch wall, nitrometer or other durable tubing.

It is not wise to overstock on rubber tubing as it may deteriorate in time, even though not in use, unless stored in an inert atmosphere such as nitrogen.

Chemicals

The chemicals required in the actual analytical operations of the Haldane apparatus are potassium hydroxide and pyrogallic acid. Carbon dioxide is absorbed by a solution of potassium hydroxide and oxygen by a mixture of solutions of potassium hydroxide and pyrogallic acid. The solutions may be purchased from some chemical supply houses or may be prepared by the user of the apparatus. The approximate quantities of the reagents, in the solid form, required for analysis of 1,000 mine-air samples are 10 pounds of potassium hydroxide and one-half pound of pyrogallic acid.

Approximately 5 pounds of mercury are required as the confining liquid in the burette and combustion pipet of the Haldane apparatus. For maximum accuracy (particularly in the determination of carbon dioxide, which is quite soluble in water), mercury should be used as the medium for displacing the air sample from its container into the analytical apparatus. Mercury may be employed for this purpose only when glass sample containers are used. Metal sample containers usually are fabricated with soldered joints, which are destroyed by amalgamation when brought into contact with mercury. A welded-steel mercury container suitable for use in connection with the displacement of air samples is shown in figure 7. A container of this type requires about 35 pounds of mercury. When considerable quantities of mercury are required, it may be advantageous to purchase it in flask (76-pound) lots.

Mercury used in the analysis of gases should be clean, and particularly should not be contaminated with caustic materials that will introduce errors in the determination of carbon dioxide and methane by premature removal of carbon dioxide from the sample in the apparatus. If the mercury used in displacing the sample from its container is contaminated with caustic material, carbon dioxide will be removed from the sample before it is introduced into the apparatus. For this reason, equipment should be available for cleaning the mercury by acid treatment. The device shown in figure 8 is convenient for this purpose. The mercury first is strained through a cloth to remove grease and floating foreign matter and then is placed in the reservoir at the top of the apparatus from which it is allowed to flow slowly through a coarse cloth or other porous material, which breaks the stream of mercury into small particles or droplets. These particles of mercury descend through the cleaning mixture (5 parts by volume of nitric acid and 95 parts of water) in the long column. The acid-scrubbed mercury collects at the seal at the bottom of the column and may be withdrawn as needed. Vacuum stills[21] or devices in which mercury is mechanically agitated in air as a purifying procedure[22] may be used in laboratories where large quantities of mercury are to be cleaned.

A supply of distilled water should be available in the laboratory for preparing solutions and for rinsing glass parts of the apparatus after cleaning. For small laboratories, it may be simpler to purchase distilled water than to install a still.

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[21] Kleiber, M., A Simple Apparatus for Mercury Distillation: Science, vol. 75, 1932, p. 196.

[22] Lawrence, J. B., Mercury the Purest Metal: Instruments, vol. 25, 1952, pp. 310-312, 363.

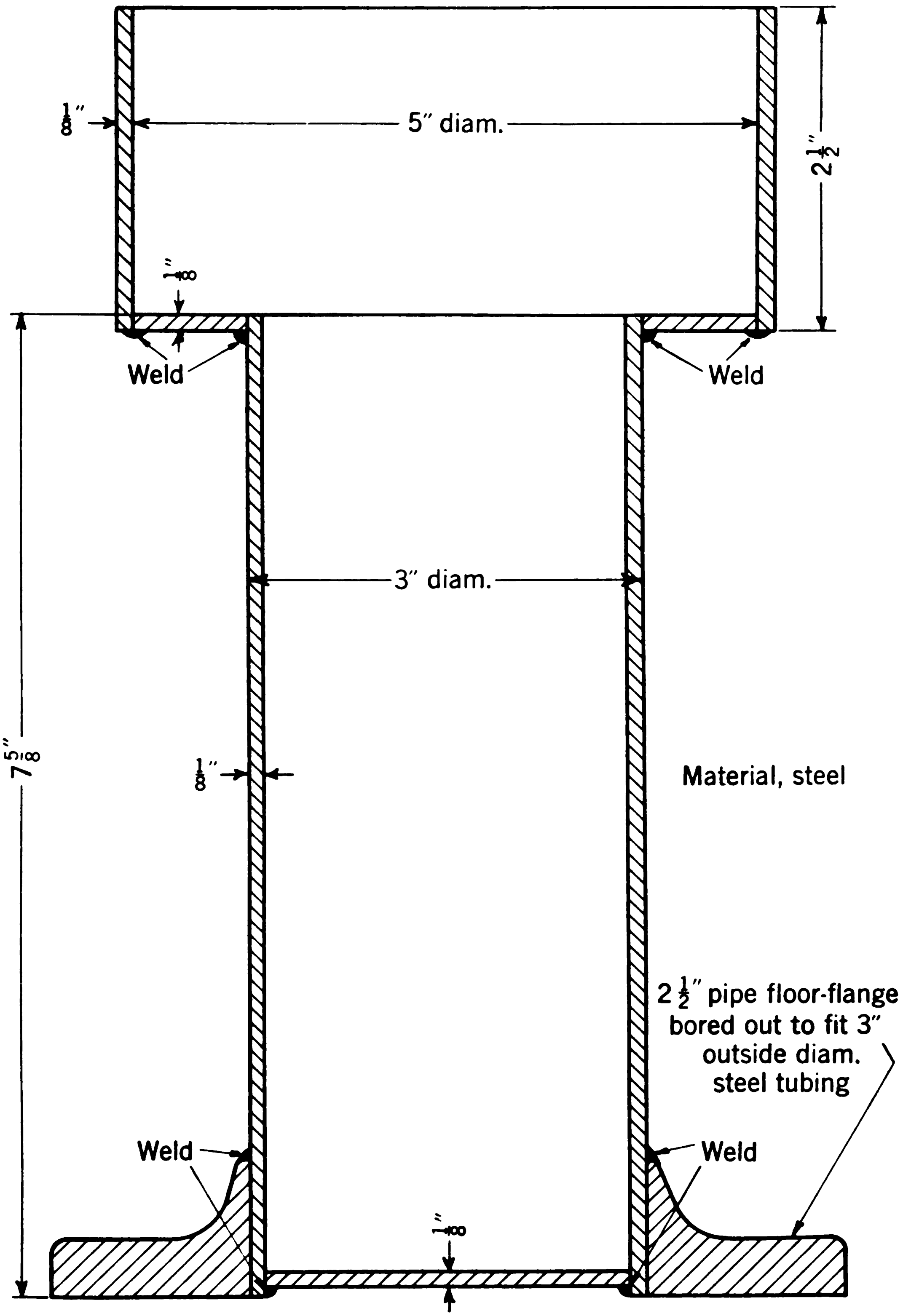

Figure 7. - Container for mercury used in displacing air samples.

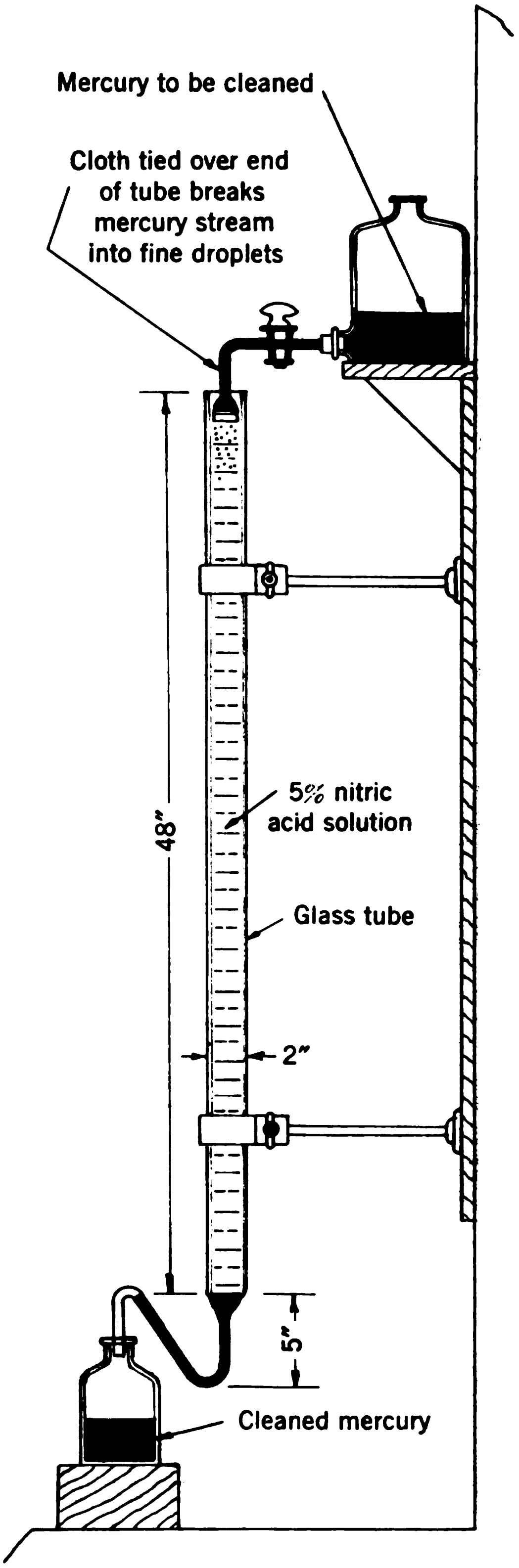

Figure 8. - Tower for acid-cleaning mercury used in gas analysis.

Nitric and sulfuric acids should be available for cleaning. A cleaning mixture of sulfuric and chromic acids is effective in removing grease films or deposits from the interior of the gas burette. One bottle each (approximately 2-1/2 liters) of nitric and sulfuric acids is the minimum supply for a small laboratory. Organic solvents, such as gasoline or benzene, never should be used in cleaning any part of the gas-analysis apparatus.

If solutions are to be prepared in the laboratory, a set of scales and weights should be provided for weighing the chemicals. A platform-type scale, commonly called a trip balance, sensitive to one-tenth gram, is suitable for this purpose.

Glassware

A supply of glass beakers should be available for preparing and dispensing solutions, adding cleaning solution or water to the gas burette, and similar purposes. Suggested sizes are 100 ml., 500 ml., and 4,000 ml. As glassware of this type is rather fragile, it is advisable to have several of each size.

Glass graduates, or measuring cylinders, are necessary in preparing solutions. Suggested sizes are 100 ml. and 1,000 ml.

Glass funnels are convenient for adding solutions to the pipets of the apparatus, for filling reagent bottles with solutions, and for similar operations.

Magnesium citrate bottles fitted with glass stoppers seating on rubber washers and held in place by spring clamps are convenient containers for storing the gas-analysis solutions. It is preferable to use several small containers rather than one large one for storing the oxygen-absorbing reagent, as in this way only a small volume of reagent comes into contact with air when the bottle is opened.

Soft glass tubing of both "shell" and "capillary" types is convenient for making connections to sample containers and for other purposes. Outside diameter of such tubing should be about 7 mm.; inside diameter of the capillary tubing should not be less than 2 mm. If the tubing is to be bent to shape in the laboratory, a Bunsen burner with a "wing" top will be needed.

Compressed Air

In operating the Haldane apparatus, low-pressure (2 to 3 pounds per square inch gage) compressed-air is needed to cool the combustion pipet and to stir the water in the jacket of the burette. If compressed air is not available at the laboratory, a small positive-pressure rotary blower driven by a fractional-horsepower motor will answer as an air supply. Such blowers may be obtained from laboratory supply houses.

Miscellaneous Materials and Tools

A supply of suitable grease is necessary to lubricate the stopcocks of the gas-analysis apparatus. As proper greasing of the stopcocks is an important part of preparing the apparatus for use, it is best to obtain a grease specially compounded for this purpose from a laboratory supply house. Ordinary pipe cleaners are useful for removing excess grease from stopcock bores, and soft cotton cloth is needed to wipe grease from the ground surfaces of stopcocks.

Triangular files, pliers, screw drivers, and soft copper wire (No. 22 B. & S. gage) will be found necessary in maintaining and adjusting the apparatus.

Portable Orsat Gas-Analysis Apparatus[23]

The portable Orsat apparatus is suitable for determining carbon dioxide, oxygen, carbon monoxide, methane, and nitrogen in the atmospheres of sealed areas or the analysis of oxygen-deficient atmospheres or considerable accumulations of carbon dioxide, methane, or nitrogen in unventilated places.

Accuracy of determination of carbon dioxide, oxygen, and carbon monoxide is 0.2 to 0.3 percent.

Methane may be determined in concentrations below, within, or above the flammable or "explosive" range with an accuracy of 0.2 to 1.0 percent, depending on the concentration of methane.

The apparatus is suitable for either laboratory or field use.

The apparatus is not suitable for accurate determination of low concentrations of methane in the air of ventilated places, such as main returns and splits, and is not suitable for determination of carbon monoxide in concentrations of less than 0.3 percent.

A number of types and designs of portable apparatus are available for analyzing various gaseous mixtures. For the analysis of mine atmospheres, the apparatus should be fitted with a straight 100 ml. burette (no bulb at top of burette) and should be suitable for determining carbon dioxide, oxygen, carbon monoxide, and methane. The first three gases are determined by absorption and methane is determined either by combustion on a heated platinum-wire coil, or by oxidation on a heated, specially prepared catalyst. In the type of apparatus using the combustion pipet a shield of wire screen or shatter-proof glass should be provided to protect the operator in event of an explosion. If the apparatus is fitted with a transformer or other electrical equipment, the purchaser should specify voltage and frequency to conform with that available in the laboratory. The combustion pipet of some types of apparatus may be operated on dry cells (No. 6) when used in the field. Such batteries should not be obtained until the apparatus actually is to be used, as they deteriorate in storage.

Many of the items listed under the Haldane apparatus are suitable for use in connection with the portable Orsat apparatus. Such items include rubber tubing, glass tubing, stopcock grease, sulfuric acid, platinum wire for the combustion pipet, and solutions for the absorption of carbon dioxide and oxygen. When the portable Orsat apparatus is used in the laboratory, many of the facilities provided for the Haldane apparatus may be used. These include power supply, compressed air for cooling the combustion pipet, and vessels in which samples are displaced from their containers. Carbon monoxide usually is determined with the portable Orsat apparatus by absorption in cuprous chloride solution. One pound of cuprous chloride (solid), one bottle (6 pounds) of chemically pure hydrochloric acid, and one-fourth pound of stannous chloride (solid) will make enough of the cuprous chloride reagent to analyze 100 to 300 samples, depending on the percentage of carbon monoxide in the samples.

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[23] Berger, L. B., and Schrenk, H. H., Sampling and Analysis of Mine Atmospheres: Bureau of Mines Miners' Circ. 34, 1948 rev., 103 pp.

The confining liquid (water) in the burette and combustion pipet of the portable Orsat apparatus is maintained in a slightly acid condition by adding sulfuric acid. A small quantity of an indicator (methyl orange) is added to the water, which colors it red so long as the water remains acid. One ounce, or even a smaller quantity, of methyl orange indicator will suffice for ordinary needs.

When the portable Orsat apparatus is used in the field, as in analyzing gases from a sealed fire area in a coal mine, the analyst also may be responsible for collecting gas samples. In such situations the sampling equipment required, in addition to suitable sample containers, consists of 4 to 6 feet of soft copper tubing (1/4-inch outside diameter) for sampling through seals, a rubber aspirator bulb for pumping gas through the sampling tube, a water gage (a glass U-tube, which may be made in the laboratory) for measuring gas pressure on seals, and suitable rubber tubing connections. Sampling techniques are discussed in detail in another Bureau of Mines publication.[24]

Laboratory-Type Orsat Apparatus[25] [26]

The laboratory-type Orsat apparatus has the same field of application as the portable Orsat, and, in addition, hydrogen and higher hydrocarbons such as ethane may be determined.

The apparatus is more accurate than the portable Orsat, but the accuracy is not adequate for determining low concentrations of methane in the air of ventilated places.

The laboratory-type Orsat apparatus suitable for the analysis of mine atmospheres usually is fitted with a straight 100-ml. burette, 3 pipets for the determination of carbon dioxide, oxygen, and carbon monoxide by absorption, and a combustion pipet for determination of methane and other combustible gases. To obtain maximum utility from this type of apparatus, it should include a tube containing copper oxide (which may be heated by an electric furnace) for the determination of carbon monoxide and hydrogen simultaneously or individually. With this arrangement, analysis may be made for four combustible gases (carbon monoxide, hydrogen, methane, and ethane). In some commercial apparatus the combustion (hot-wire) pipet is replaced by a tube of specially prepared catalyst for combustion of methane and ethane. For maximum accuracy, mercury should be used as the confining liquid in burette and combustion pipet or tube. In the type of apparatus employing the combustion pipet, a shield of wire screen or shatter-proof glass should be provided to protect the operator in event of an explosion. Electrical accessories should be specified, in regard to type of current, voltage, and frequency, to conform with the power supply available in the laboratory.

Many of the items mentioned in connection with the Haldane and portable Orsat types are suitable for use with the laboratory-type Orsat. These include rubber tubing, stopcock grease, cleaning solutions, sample-displacement vessels, compressed-air for cooling the combustion pipet and copper oxide tube, and reagents for the absorption of carbon dioxide and oxygen.[27] Cuprous chloride solution may be used for the absorption of carbon monoxide, although a preferred reagent for this purpose in the laboratory-type Orsat is composed of cuprous sulfate, beta-naphthol, and sulfuric acid.[28 29] This reagent may be purchased already prepared from some laboratory supply houses that specialize in gas-analysis equipment.

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[24] See work cited in footnote 23 (p. 38).

[25] Burrell, G. A., and Seibert, F. M. (rev. by G. W. Jones), The Sampling and Examination of Mine Gases and Natural Gas: Bureau of Mines Bull. 197, 1926, 108 pp.

[26] Fieldner, A. C., Jones, G. W., and Holbrook, W. F., The Bureau of Mines Orsat Apparatus for Gas Analysis: Bureau of Mines Tech. Paper 320, 1925, 18 pp.

Pyrotannic Method for Determining Carbon Monoxide[30 31 32]

The pyrotannic acid method is suitable for determining low concentrations (0.01 to 0.20 percent) of carbon monoxide in the air of ventilated places or in the gases from sealed fire areas when the fire is nearly extinguished and the area is cooling. The method may be considered specific for carbon monoxide in mine air samples, as the color reaction involved depends on the reaction of carbon monoxide with the hemoglobin of blood.

The accuracy of the method is 0.01 in the range 0.00 to 0.05 percent of carbon monoxide, 0.02 in the range 0.05 to 0.10 percent, and 0.03 in the range 0.10 to 0.20 percent. When blood from one source is used in the test medium for both a "blank" or control specimen for comparison purposes and as the reagent for analyzing an air sample, a blood saturation of 10 percent (equivalent to 0.01 percent of carbon monoxide in air) is readily evident to persons with normal color perception and traces below this concentration may be detected.

The method is suitable, also, for determining carbon monoxide in the blood of persons overcome or killed by that gas.

The method is suitable for use in the field as well as in the laboratory.

The method is particularly suitable for occasional use or in laboratories where only a few samples are to be analyzed for carbon monoxide.

The pyrotannic apparatus may be purchased as an essentially complete unit consisting of color standards, blood lancet, blood-dilution pipet, required test tubes, and a supply of the pyrotannic reagent. This reagent consists of equal parts, by weight, of pyrogallic and tannic acids thoroughly mixed and ground together to a fine powder. One ounce of each of the ingredients will make enough of the mixture to conduct more than 1,000 tests or analyses. The mixed reagent must be kept in a tightly stoppered bottle, as it will absorb moisture from the air. In the analysis of air samples by the pyrotannic-acid method, any glass bottle that may be stoppered tightly will serve as a sample container. The volume of the sample bottles must be known, however, as volume of sample enters into the calculation of the percentage of carbon monoxide in the air sample. Bottles of 100- to 250-ml. capacity generally are used, but containers of smaller volume may be used if the supply of sample is limited.

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[27] See Preparation of Solutions, under section on Haldane-Type Gas Analysis Apparatus.

[28] Work cited in footnote 23 (p.38).

[29] Berger, L. B., and Schrenk, H. H., Methods for the Detection and Determination of Carbon Monoxide: Bureau of Mines Tech. Paper 582, 1938, 30 pp. (Rev. 1954. To be published.)

[30] Sayers, R. R., and Yant, W. P., The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and in Air; Its Use in the Diagnosis and Investigation of Cases of Carbon Monoxide Poisoning: Bureau of Mines Tech. Paper 373, 1927, 18 pp.

[31] Work cited in footnote 29.

[32] Forbes, J. J., and Grove, G. W., (rev. by McElroy, G. E., Watson, H. A., Coggeshall, E. J., Dornenburg, D. D., and Berger, L. B.), Mine Gases and Methods for Detecting Them: Bureau of Mines Miners' Circ. 33, 1954, 82 pp.

"Phosphomolybdic Acid" Method for Determining Carbon Monoxide[33]

The phosphomolybdic acid method is suitable for determining low concentrations (0.002 to 0.06 percent) of carbon monoxide in the air of ventilated places or in the gases from sealed fire areas when the fire is nearly extinguished and the area is cooling.

The method is more sensitive and accurate than the pyrotannic acid method for carbon monoxide but is more complicated in respect to apparatus and technique.

The method is best adapted to use in laboratories where a considerable number of samples are to be analyzed for carbon monoxide and where the method is in more or less continuous use.

The method is not suitable for field use.

A list of equipment for determining carbon monoxide by the phosphomolybdic acid method is not included in this publication, as the reference cited contains this information in detail.

Phenoldisulfonic Acid Method for Determining Oxides of Nitrogen[34]

The phenoldisulfonic acid method is suitable for determining total toxic oxides of nitrogen in concentrations that may be encountered (a) in the air of working places after blasting, (b) as a result of the use of internal combustion (diesel) engines, or (c) in comparatively high concentrations such as may be present in the undiluted exhaust gases of internal combustion engines.

The method necessitates collecting samples in specially prepared containers.

The analytical procedure may be conducted only in a laboratory.

Reagents

The following reagents are required in determining oxides of nitrogen in mine air samples:

Potassium hydroxide.

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[33] Polis, B. D., Berger, L. B., and Schrenk, H. H., Colorimetric Determination of Low Concentrations of Carbon Monoxide by Use of a Palladium Chloride-Phosphomolybdic Acid-Acetone Reagent: Bureau of Mines Rept. of Investigations 3785, 1944, 13 pp.

[34] Beatty, R. L., Berger, L. B., and Schrenk, H. H., Determination of the Oxides of Nitrogen by the Phenoldisulfonic Acid Method: Bureau of Mines Rept. of Investigations 3687, 1943, 17 pp.

Phenoldisulfonic acid reagent, which is prepared from concentrated sulfuric acid, fuming sulfuric acid, and phenol.

Litmus or other indicating test paper.

Ammonium hydroxide.

Potassium nitrate.

Distilled water.

Specially prepared glass containers are necessary in collecting samples for determining oxides of nitrogen. It is possible that these containers, already prepared, may be obtained from laboratory supply houses that specialize in gas-analysis equipment. If the containers are to be prepared in the laboratory, the following reagents will be required:

Tenth-normal sulfuric acid solution, reagent grade.

Hydrogen peroxide, 30 percent, reagent grade.

The specially prepared sample containers (see fig. 3) are intended primarily to furnish a simple and convenient method for sampling underground atmospheres for determining oxides of nitrogen. Preparation of such containers requires glass-blowing facilities and a pump for evacuating the container before it is sealed. Other means suitable for collecting the samples may be devised if these facilities are not available.

A small rubber cap is used to seal the vacuum-type container for oxides of nitrogen after the sample has been collected. These caps are known as rubber policemen in the laboratory parlance and may be obtained from laboratory supply houses.

Apparatus

In the analytical procedure, the following equipment is required:

Glass beakers of 150-ml. capacity, into which the liquid absorbent from the sample container is transferred.

Cover glasses to fit the above beakers. These are to prevent possible loss of material from the beakers when their contents are evaporated, and to prevent the entrance of foreign material that might contaminate the contents of the beaker.

An electric hotplate for the evaporation procedure.

Graduates and pipets suitable for measuring reagent volumes.

The final step in determining oxides of nitrogen is a comparison of the intensity of color produced by chemical treatment of the samples, with the color of "standards" similarly processed. The comparison may be made visually by matching the colors in Nessler tubes to which the colored solutions are transferred. This method is the simplest and least expensive for the small laboratory, where only a limited number of samples are to be analyzed for oxides of nitrogen. When a greater number of analyses are to be made, a colorimeter of the photoelectric type is preferable, as an instrument of this type eliminates visual fatigue in color perception, which is particularly notable in judging the intensity of the pale yellows that are produced in this analytical procedure. A colorimeter of this type may be used to advantage also in determining carbon monoxide by the phosphomolybdic acid method referenced in this circular.

Other methods are available for determining certain toxic oxides of nitrogen[35] and for the specific determination of nitrogen dioxide.[36]

Gas Analysis by Infrared Absorption

Certain components of gaseous mixtures may be determined by measuring their ability to absorb infrared radiation. Compounds such as carbon dioxide, carbon monoxide, water vapor, methane, and other hydrocarbons absorb infrared radiation, whereas symmetrical diatomic gases such as oxygen, nitrogen, and hydrogen do not. The infrared wavelength, or frequency of vibration, at which different compounds absorb depends on the mass of the atoms in the compound, their geometrical spacing, and the chemical bond forces between the atoms that constitute the compound. These characteristics of a molecular species determine the natural frequency of vibration of the atoms that constitute that compound. When infrared radiation of the same frequency or wavelength is imposed upon the compound, absorption of the infrared energy occurs; when infrared energy of other frequencies is imposed upon the same gaseous compound absorption does not occur. Thus, different compounds exhibit characteristic absorption behavior when subjected to infrared radiation, and it is upon this principle that gas analysis by infrared absorption is based.

In application of this principle, a beam of infrared radiation from a suitable source (usually an electrically heated resistance element or glower) is passed through a cell that contains the gas sample under examination and then is directed through an optical path to a detecting element that measures the intensity or energy of the radiation that emerges from the cell as compared to the energy of the beam that enters the cell. Thus, a means is obtained for measuring the capacity of the gas or gases in the analyzing cell to absorb infrared radiation. Since infrared radiation lies within the heat portion of the spectrum of vibration frequencies, the detecting element is a heat-sensitive device (for example, a thermocouple or bolometer) that is capable of absorbing heat energy and transforming it into electrical energy that may be amplified and recorded. Various schemes have been developed for applying this basic principle to analysis by infrared absorption.

In the dispersion-type infrared spectrometer the radiation that passes through the gas sample is separated or dispersed by a continuously variable element of the optical system, such as a prism rotating through an arc so that at a given time the degree of infrared absorption is measured at only one particular wavelength or a very narrow band of wavelengths. Thus, the characteristic absorption pattern of a particular compound may be determined in respect to the wavelengths at which that compound absorbs the infrared. In this manner different gases in a mixture may be identified by their characteristic behavior, and the concentration of a particular constituent of the mixture may be determined by measuring the magnitude of absorption at the wavelength, or wavelengths, at which that gas is known to exhibit an absorption maximum or peak.

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[35] Patty, F. A., and Petty, G. M., Nitrite Field Method for the Determination of Oxides of Nitrogen (Except N_2O and N_2O_5): Jour. Ind. Hyg. and Toxicol., vol. 25, 1943, pp. 361-365.

[36] Saltzman, B. E., Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere: Anal. Chem., vol. 26, 1954, pp. 1949-1955.

In the nondispersion-type analyzer two beams of infrared radiation are passed through a cell that contains the gas mixture under examination, and also through cells that contain certain components of the mixture which absorb or filter out portions of the infrared spectrum to obtain selectivity and make it possible to determine a single constituent of the gas mixture. The finally emerging radiation is measured by suitable detecting elements. Various modifications of this filtration principle are possible, and have been employed to obtain selectivity and a high degree of sensitivity in response.

The dispersion-type infrared spectrometer is primarily a laboratory instrument for the qualitative identification of certain components of gaseous mixtures and for the quantitation of components thus identified. The nondispersion-type analyzer is primarily adaptable to the examination of mixtures of known qualitative composition and is applicable in this field not only in the laboratory but also in plant operations where continuous control analysis of products is desired.

The foregoing discussion of gas analysis by infrared absorption is merely a very brief presentation of the principles involved. Discussion of the theory of infrared absorption or detailed description of instruments that have been developed for this method of analysis are not within the scope of this circular.

LABORATORY PLAN

The required size or floor space of the gas-analysis laboratory will depend, of course, on the volume and variety of analytical work to be done. In general, the equipment is best housed in a separate room used only for gas analysis. The room should be arranged so that it is free of cross drafts and not subject to sudden changes of temperature. Facilities such as electric power, tap water, compressed air, and fuel gas should be available.

In addition to a suitable bench for mounting the gas-analysis apparatus, the laboratory equipment should include a flattop table or bench that may be used in preparing solutions or for analytical work, a sink, shelves for storing chemicals and gas-sample containers, and lockers in which spare glass parts of the gas-analysis apparatus may be stored. Means should be provided for orderly filing of sample records and analytical results.

The method of mounting the gas-analysis apparatus will depend on the structural features of the particular equipment obtained. The Haldane-type apparatus or the laboratory Orsat should be more or less permanently installed on a stout table or bench that will not be subject to shock or vibration. The apparatus should be located so that it is not subject to sudden changes in temperature, as by drafts from open doors or windows or by excessive heat from room-heating appliances.

Figure 9 shows the design of a bench for gas-analysis apparatus used in the Gas Analysis Laboratory of the Bureau of Mines. The figure shows a section of bench suitable in size for mounting one apparatus; the length of bench may be increased to accommodate any desired number of units, and for a large laboratory, apparatus may be mounted on both sides of the bench.

The figure as drawn represents the mounting of a Haldane-type apparatus, but the laboratory-type Orsat may be installed similarly. The manifold, pipets, and electrical controls are attached to panel _a_; the burette is supported by clamps attached to rod _b_; the leveling bulb is supported on rod _c_. Rods _b_ and _c_ are clamped to the pipe framework, _d_, which extends the length of the bench and permits

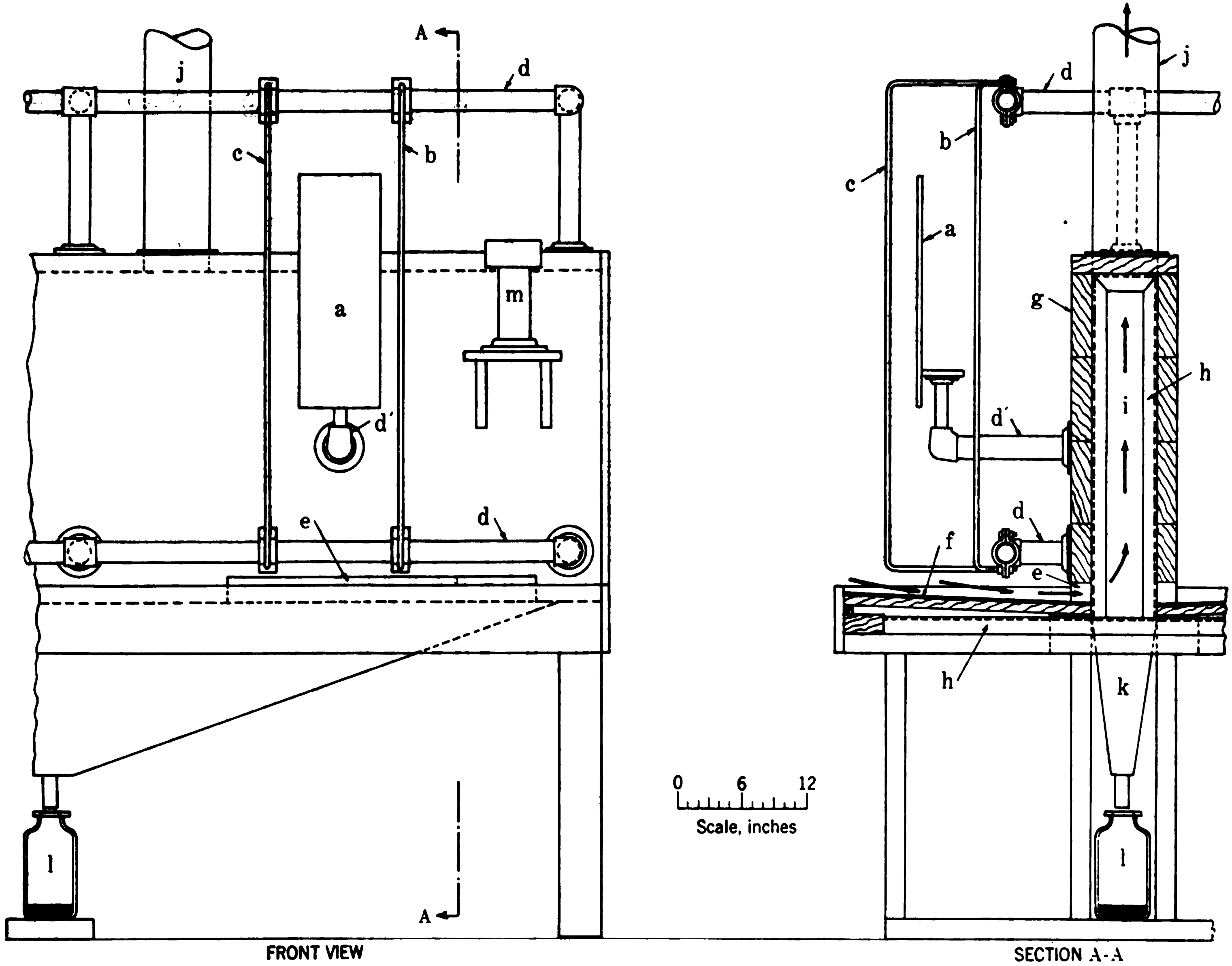

Figure 9. - Bench for gas analysis apparatus, as used in Bureau of Mines gas-analysis laboratory.

lateral adjustment of the rods to any desired position. It may be noted that panel a is supported on a short length of pipe, d', attached to the center partition, g, as are frames, d, and a shelf for the sample-displacement vessel, m. With this system of mounting, the bench top, f, is left clear of apparatus supports, and spilled mercury may be removed by brushing it from the bench top, which slopes slightly to the rear, into the slot, e, from which it drops into welded-steel trough, k, and thence into reservoir l, from which it may be recovered.

As some potential health hazard may exist from inhaling mercury vapor in a laboratory where this material is used, provision should be made for ventilation of the gas-analysis laboratory. The most prolific sources of mercury vapor are the fine droplets of mercury that are formed when it is spilled on the bench top. Accordingly, ventilation is most effective if provided at that level rather than by an overhead hood or by general ventilation of the room. As shown in figure 9, the center partition, g, is hollow, being formed of 2-inch plank bolted to channel-iron frames, h. The enclosed space, i, communicates through duct j with an exhaust fan, so that a continuous stream of air is drawn over the bench top and into i through the slot, e, as shown by the heavy arrows in the figure. In the Gas Analysis Laboratory of the Bureau of Mines, approximately 250 cubic feet per minute of ventilating air is provided in this manner for each gas-analysis apparatus, and tests of the laboratory air have shown it to be essentially free of mercury vapor.

As shown in figure 9, approximately 3-1/2 feet of bench are required for an apparatus, and a clear floor space of at least 3-1/2 by 3-1/2 feet should be provided in front of the bench for the operator.

APPENDIX: ACCURACY OF DETERMINATION OF METHANE WITH THE HALDANE GAS ANALYSIS APPARATUS

Test mixtures of methane in air were accurately prepared by adding measured volumes of methane to a chamber of known volume. The purity of the methane was established by chemical and mass-spectrographic analyses. The volume of the chamber (926 cubic feet) was calculated from 3 sets of measurements made independently by 3 persons. The volumes of methane were measured carefully with a calibrated, wet-type test meter and were corrected for water vapor content at the existing temperature. Three concentrations of methane in air were prepared: (1) 0.25, (2) 0.23, and (3) 0.27 percent by volume. Twenty-five samples from the first test mixture and ten from each of the other test mixtures were collected in vacuum-type sampling tubes and sealed with wax-filled caps in the manner used conventionally by Bureau of Mines coal-mine inspectors. The sample bottles from the three mixtures purposely were intermixed before introducing into the laboratory and were treated as routine samples from coal mine inspections, except that multiple analyses were made.

Each sample, with the exception of sample No. 14 which was accidentally destroyed after 4 analyses, was analyzed 6 times in duplicate by each of 3 analysts. Sample 10 from mixture 1 was broken accidentally before any analyses were performed.

Twelve analysts each using a different Haldane apparatus performed the analyses. The number of individual determinations of methane by a particular analyst (hence per apparatus) ranged from 14 to 32. The analysts had no previous knowledge of the composition of the prepared test mixtures and, because of the mixed order of numbering the samples, would have been unable to associate any individual sample with a particular test mixture.

The concentration of methane was calculated on a volume basis as follows:

Volume of methane in sample =

$$\frac{\text{contraction caused by combustion + carbon dioxide formed}}{3}$$

$$\text{Percent, by volume, of methane} = \frac{\text{volume of methane}}{\text{original volume of sample}} \times 100$$

Table 2 shows the experimentally determined methane concentration obtained in each analysis, the average concentration for each sample tube from which six analyses were made, and the overall average of the samples from each test mixture.

Table 3 shows the averages of pairs of determinations by individual Haldane apparatus of methane concentration in each sample from the three known methane-air mixtures.

Table 4 shows the averages of 4 determinations - the possible combinations of pairs of determinations from a given sample by 2 individual apparatuses - of methane concentration in each sample from the 3 known methane-air mixtures.

Table 5 shows the frequency distribution of experimentally determined methane values expressed in relation to deviation in percent, by volume, of methane from the true methane content.

TABLE 2. - Summary of analytical results showing individual determinations of methane concentration in each sample from three test mixtures containing known concentrations of methane in air

Sample No.	Test mixture No. 1: 0.25 percent methane in air						
	Methane by analysis, percent by volume						
	Individual determinations						
	Pair (1)		Pair (2)		Pair (3)		Average
4	0.25	0.24	0.25	0.24	0.24	0.24	0.24
7	.24	.24	.25	.25	.24	.26	.25
8	.25	.24	.25	.25	.26	.25	.25
9	.25	.24	.25	.25	.24	.25	.25
13	.25	.25	.24	.24	.25	.25	.25
14	.26	.25	.25	.24	--	--	--
17	.25	.24	.25	.25	.24	.23	.24
18	.24	.24	.25	.24	.25	.25	.25
19	.25	.25	.26	.26	.26	.24	.25
20	.25	.25	.26	.27	.24	.23	.25
23	.25	.25	.24	.25	.25	.24	.25
24	.25	.26	.24	.26	.24	.24	.25
27	.24	.25	.24	.24	.25	.26	.25
28	.24	.25	.23	.25	.22	.23	.24
29	.25	.24	.25	.25	.24	.24	.25
30	.24	.25	.25	.25	.25	.25	.25
33	.24	.24	.25	.25	.26	.26	.25
34	.24	.24	.26	.26	.25	.25	.25
35	.24	.25	.26	.26	.26	.25	.25
38	.26	.25	.25	.25	.24	.25	.25
39	.25	.25	.26	.25	.25	.25	.25
40	.25	.25	.26	.25	.25	.25	.25
44	.25	.25	.25	.25	.25	.25	.25
45	.25	.26	.25	.25	.26	.26	.26

	Percent		Percent
Minimum individual determination:	0.22	Average:	0.25
Maximum individual determination:	0.27		

	Percent
Minimum average of an individual sample:	0.24
Maximum average of an individual sample:	0.26

Sample No.	Test mixture No. 2: 0.23 percent methane in air						
	Methane by analysis, percent by volume						
	Individual determinations						
	Pair (1)		Pair (2)		Pair (3)		Average
1	0.23	0.23	0.22	0.22	0.22	0.23	0.23
2	.26	.25	.22	.22	.23	.23	.24
3	.23	.24	.24	.23	.21	.23	.23
11	.23	.22	.22	.21	.24	.21	.22
12	.24	.22	.23	.23	.23	.21	.23
21	.23	.23	.22	.21	.22	.22	.22
22	.23	.23	.22	.22	.23	.24	.23
31	.23	.22	.23	.22	.24	.22	.23
32	.26	.24	.22	.22	.23	.22	.23
37	.22	.22	.21	.23	.22	.24	.22

	Percent		Percent
Minimum individual determination:	0.21	Average:	0.23
Maximum individual determination:	0.26		

	Percent
Minimum average of an individual sample:	0.22
Maximum average of an individual sample:	0.24

Sample No.	Test mixture No. 3: 0.27 percent methane in air						
	Methane by analysis, percent by volume						
	Individual determinations						
	Pair (1)		Pair (2)		Pair (3)		Average
5	0.26	0.26	0.27	0.26	0.26	0.26	0.26
6	.26	.26	.30	.29	.26	.26	.27
15	.26	.26	.26	.26	.27	.27	.26
16	.28	.27	.25	.27	.26	.26	.27
25	.26	.25	.27	.27	.26	.28	.27
26	.26	.24	.28	.26	.26	.26	.26
36	.26	.26	.26	.27	.28	.27	.27
41	.27	.27	.26	.26	.27	.26	.27
42	.27	.27	.27	.27	.26	.27	.27
43	.25	.26	.26	.26	.28	.28	.27

	Percent		Percent
Minimum individual determination:	0.24	Average:	0.27
Maximum individual determination:	0.30		

	Percent
Minimum average of an individual sample:	0.26
Maximum average of an individual sample:	0.27

TABLE 3. - Summary of analytical results showing averages of pairs of determinations by individual Haldane apparatus of methane concentration in each sample from three known methane-air mixtures

Test mixture No. 1: 0.25 percent methane in air				Test mixture No. 2: 0.23 percent methane in air				Test mixture No. 3 0.27 percent methane in air			
Sample No.	CH$_4$, percent by volume: Average of pairs			Sample No.	CH$_4$, percent by volume: Average of pairs			Sample No.	CH$_4$, percent by volume: Average of pairs		
	Pair(1)	Pair(2)	Pair(3)		Pair(1)	Pair(2)	Pair(3)		Pair(1)	Pair(2)	Pair(3)
4	0.25	0.25	0.24	1	0.23	0.22	0.23	5	0.26	0.27	0.26
7	.24	.25	.25	2	.26	.22	.23	6	.26	.30	.26
8	.25	.25	.26	3	.24	.24	.22	15	.26	.26	.27
9	.25	.25	.25	11	.23	.22	.23	16	.28	.26	.26
13	.25	.24	.25	12	.23	.23	.22	25	.26	.27	.27
14	.26	.25	--	21	.23	.22	.22	26	.25	.27	.26
17	.25	.25	.24	22	.23	.22	.24	36	.26	.27	.28
18	.24	.25	.25	31	.23	.23	.23	41	.27	.26	.27
19	.25	.26	.25	32	.25	.22	.23	42	.27	.27	.27
20	.25	.27	.24	37	.22	.22	.23	43	.26	.26	.28
23	.25	.25	.25								
24	.26	.25	.24								
27	.25	.24	.26								
28	.25	.24	.23								
29	.25	.25	.24								
30	.25	.25	.25								
33	.24	.25	.26								
34	.24	.26	.25								
35	.25	.26	.26								
38	.26	.25	.25								
39	.25	.26	.25								
40	.25	.26	.25								
44	.25	.25	.25								
45	.26	.25	.26								

TABLE 4. - Summary of analytical results showing averages of 4 determinations (2 each on 2 individual Haldane apparatus) of methane concentration in each sample from 3 known methane-air mixtures. The values of individual determinations contributing to the pair averages shown in table 3 were used to compute averages of two pairs

Test mixture No. 1: 0.25 percent methane in air				Test mixture No. 2: 0.23 percent methane in air				Test mixture No. 3: 0.27 percent methane in air			
	CH$_4$, percent by volume: Averages of two pairs (4 determinations)				CH$_4$, percent by volume: Averages of two pairs (4 determinations)				CH$_4$, percent by volume: Averages of two pairs (4 determinations)		
Sample No.	Pairs(1) and (2)	Pairs(1) and (3)	Pairs(2) and (3)	Sample No.	Pairs(1) and (2)	Pairs(1) and (3)	Pairs(2) and (3)	Sample No.	Pairs(1) and (2)	Pairs(1) and (3)	Pairs(2) and (3)
4	0.25	0.24	0.24	1	0.23	0.23	0.22	5	0.26	0.26	0.26
7	.25	.25	.25	2	.24	.24	.23	6	.28	.26	.28
8	.25	.25	.25	3	.24	.23	.23	15	.26	.27	.27
9	.25	.25	.25	11	.22	.23	.22	16	.27	.27	.26
13	.25	.25	.25	12	.23	.23	.23	25	.26	.26	.27
14	.25	--	--	21	.22	.23	.22	26	.26	.26	.27
17	.25	.24	.24	22	.23	.23	.23	36	.26	.27	.27
18	.24	.25	.25	31	.23	.23	.23	41	.27	.27	.26
19	.26	.25	.26	32	.24	.24	.22	42	.27	.27	.27
20	.26	.24	.25	37	.22	.23	.23	43	.26	.27	.27
23	.25	.25	.25								
24	.25	.25	.25								
27	.24	.25	.25								
28	.24	.24	.23								
29	.25	.24	.25								
30	.25	.25	.25								
33	.25	.25	.26								
34	.25	.25	.26								
35	.25	.25	.26								
38	.25	.25	.25								
39	.25	.25	.25								
40	.25	.25	.25								
44	.25	.25	.25								
45	.25	.26	.26								

TABLE 5. - Frequency distribution of experimentally determined methane values expressed in relation to deviation in percent, by volume, of methane from the true methane content of three known methane-air mixtures

Test mixture number and known concentration		Single methane determination		Average of two methane determinations--on same apparatus		Average of 4 methane determinations--2 on each of 2 different apparatuses		Average of 6 methane determinations--2 on each of 3 different apparatuses	
		Number	Percent of total	Number	Percent of total	Number	Percent of total	Number	Percent of total
1 (0.25 percent methane)	True value +0.03	0	0	0	0	0	0	0	0
	True value + .02	1	.7	1	1.4	0	0	0	0
	True value + .01	23	16.2	14	19.7	8	11.4	1	4.3
	True value	74	52.1	43	60.6	51	72.9	19	82.7
	True value - .01	39	27.5	12	16.9	10	14.3	3	13.0
	True value - .02	4	2.8	1	1.4	1	1.4	0	0
	True value - .03	1	.7	0	0	0	0	0	0
	Total	142	100.0	71	100.0	70	100.0	23	100.0
2 (0.23 percent methane)	True value +0.03	2	3.3	1	3.3	0	0	0	0
	True value + .02	1	1.7	1	3.3	0	0	0	0
	True value + .01	8	13.3	3	10.0	5	16.7	1	10.0
	True value	21	35.0	14	46.7	18	60.0	6	60.0
	True value - .01	22	36.7	11	36.7	7	23.3	3	30.0
	True value - .02	6	10.0	0	0	0	0	0	0
	True value - .03	0	0	0	0	0	0	0	0
	Total	60	100.0	30	100.0	30	100.0	10	100.0
3 (0.27 percent methane)	True value +0.03	1	1.7	1	3.3	0	0	0	0
	True value + .02	1	1.7	0	0	0	0	0	0
	True value + .01	6	10.0	3	10.0	2	6.7	0	0
	True value	17	28.3	11	36.7	15	50.0	7	70.0
	True value - .01	31	51.6	14	46.7	13	43.3	3	30.0
	True value - .02	3	5.0	1	3.3	0	0	0	0
	True value - .03	1	1.7	0	0	0	0	0	0
	Total	60	100.0	30	100.0	30	100.0	10	100.0
1, 2, and 3 composite	True value +0.03	3	1.1	2	1.5	0	0	0	0
	True value + .02	3	1.1	2	1.5	0	0	0	0
	True value + .01	37	14.1	20	15.3	15	11.5	2	4.7
	True value	112	42.8	68	52.0	84	64.6	32	74.4
	True value - .01	92	35.1	37	28.2	30	23.1	9	20.9
	True value - .02	13	5.0	2	1.5	1	0.8	0	0
	True value - .03	2	.8	0	0	0	0	0	0
	Total	262	100.0	131	100.0	130	100.0	43	100.0

In table 5, from left to right, it is evident that the limits of deviation of experimentally determined methane values from the true values became narrower as the number of determinations used for computing the methane content was increased. In other words, the greater the number of determinations made, the closer the experimentally determined average value was to the true methane content of the test mixture. In these tests it was found: (1) Any single determination of methane might vary from the true value by ±0.03 percent, by volume; (2) the average of two methane determinations by an individual apparatus might vary from the true value by ±0.02 to ±0.03 percent, by volume; (3) the average of 4 methane determinations - 2 each by 2 individual apparatus - might vary from the true value by ±0.01 percent (1 value out of 130 showed a deviation of -0.02 from the true value); (4) the average of 6 methane determinations - 2 each by 3 individual apparatus - might vary from the true value by ±0.01 percent, by volume.

The discussion above relates to the maximum variations observed in these tests. Examination of the frequency of occurrence of experimental values in relation to the positive and negative deviations from the true values shows that for the 3 test mixtures experimental average values based on 4 or 6 determinations agreed with the known values in 50 to 83 percent of the cases, or, if the results for the 3 test mixtures be combined, the averages of 4 to 6 determinations agreed with the known values in 65 to 74 percent of the cases. In those instances where deviation from the true value did occur, the experimentally determined values were low more frequently than high.